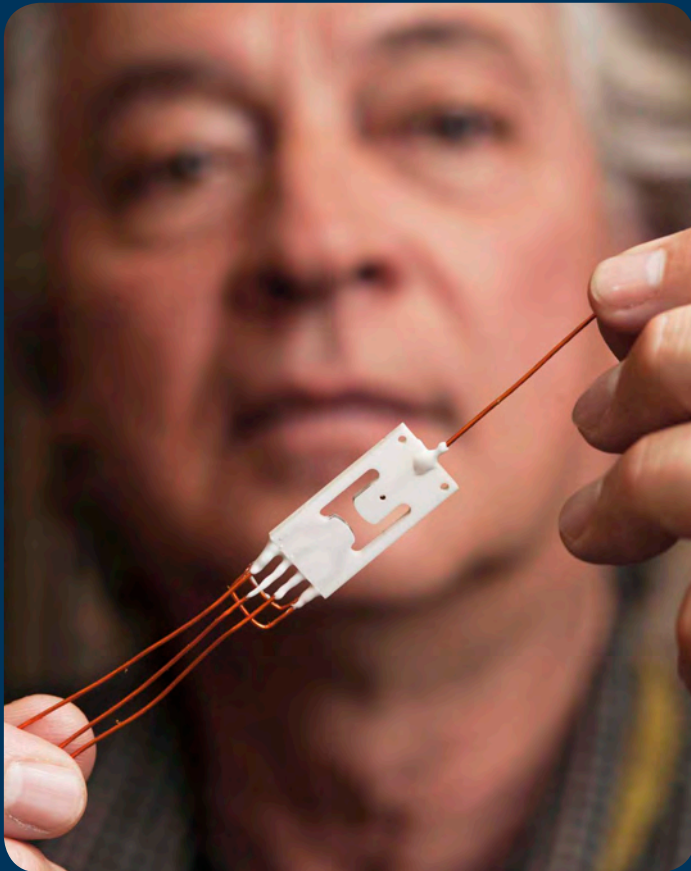
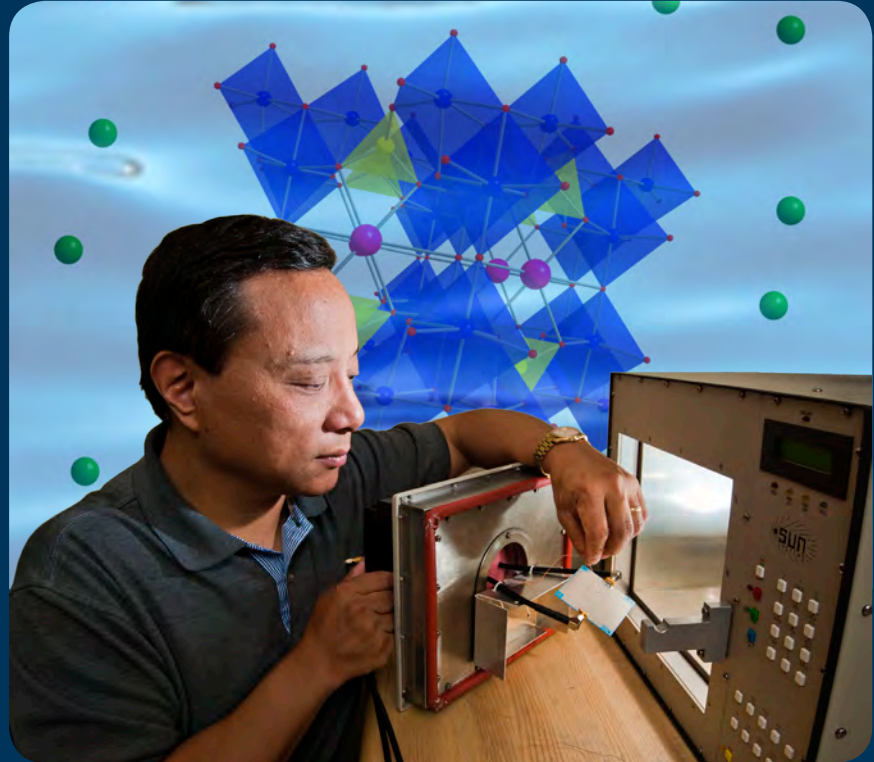




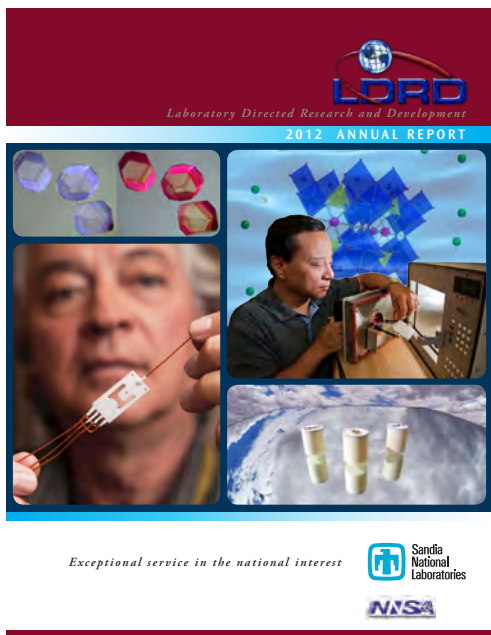
Laboratory Directed Research and Development

2012 ANNUAL REPORT



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Cover photos:

Clockwise from Upper Left:

- Crystals of Metal Organic Frameworks (MOFs), substances that act as molecular nanocages in which other molecular species can be trapped for diverse applications, such as the microcantilevers developed in project 141691
- Sandian Steve Dai prepares his low-temperature co-fired localized temperature stable dielectric developed in project 148900
- Tamper-resistant miniaturized system for capturing atmospheric samples for analysis, developed in project 151318, with each sampler about the size of an earplug.
- Sandian Juan Elizondo-Decanini displays his miniature tritium-free solid-state neutron generator developed in project 158850.

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Abstract

This report summarizes progress from the Laboratory Directed Research and Development (LDRD) program during fiscal year 2012. In addition to a programmatic and financial overview, the report includes progress reports from 433 individual R&D projects in 10 categories. Information for 163 projects in their final year is presented in a more-comprehensive format, while for those 270 in pre-final years, only an abstract is presented herein.



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 - 486 MEMS Photoacoustic Spectroscopy
 - 487 AF&F Fail-Safe Feature for Abnormal Thermal Environments using Shape-Memory Alloys
 - 488 New Composite Separator Pellet to Increase Power Density and Reduce Size of Thermal Batteries
 - 489 Liquid-Metal Environment Sensing Devices (ESDs)
 - 490 Novel Failure Analysis Technique for Defect or Precursor Detection
 - 491 Imaging and Quantification of Hydrogen-Isotope Trapping in Stainless Steels
 - 493 Developing a Multiscale Test Approach for Characterizing NW Polymer Composites
 - 495 Exploring Formal Verification Methodology for FPGA-Based Digital Systems
 - 497 A Novel Bi-Functional Conducting-Polymer Sensor Material
 - 499 Ultrafast Laser Diagnostics to Investigate Initiation Fundamentals in Energetic Materials
 - 500 Ion-Induced Secondary Electron Emission and Vacuum Surface Flashover for High Gradient Ion Beam Accelerators
 - 501 Determination of Reaction-Zone Length in Vapor-Deposited Explosive Films
 - 502 Gas Permeation Properties of Graphene Membranes
 - 503 Chemical Enhancement of Surface Kinetics in Hydrogen Storage Materials
 - 504 Advances in High-Dynamic-Range Resonant Accelerometers
 - 505 Impact of Crystallization on Glass-Ceramic-to-Metal Bonding
 - 506 Synthesis of Wear-Resistant Electrical-Contact Materials by Physical Vapor Deposition
 - 507 Extension of Semiconductor Laser Diodes to New Wavelengths for Novel Applications
 - 508 Deciphering the Role of Residual Stresses on the Strength of Adhesive Joints
 - 509 Inherent Secure Communication Using Lattice-Based Waveform Design
 - 510 Impact of Materials Processing on Microstructural Evolution and Hydrogen-Isotope-Storage Properties of Pd-Rh Alloy Powders
 - 511 Developing Software Systems for High-Assurance Applications

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- 513 Hybrid Methods for Cybersecurity Analysis
- 514 Investigate the Effectiveness of Many-Core Network Processors for High- Performance Cyber Protection Systems
- 516 Leveraging Complexity for Unpredictable yet Robust Cyber Systems
- 517 Massive-Scale Graph Analysis on Advanced Many-Core Architectures
- 519 Proactive Defense for Evolving Cyber Threats
- 521 Detection of Identifiable Data
- 522 Reliable PUFs for Supply Chain Assurance
- 523 Uncertainty Quantification and Substantiation for Machine Learning in the Context of Cybersecurity
- 524 Assessing Vulnerabilities of Reconfigurable Logic RF Systems
- 525 Peering through the Haze: Privacy and Monitoring in the Cloud Computing Paradigm
- 526 Secure and Efficient Privacy Preserving Program Obfuscation with Oblivious RAM
- 527 Advanced Malware Analytics
- 528 Instrumenting Nation-Scale Networks with Hierarchical, Peer-to-Peer Communications
- 529 Memristor Evaluation and Optimization for Cybersecurity
- 530 A Thin Hypervisor for Dynamic Analysis of ARM Based Embedded Systems
- 531 Encryption using Electrochemical Keys (EEK)
- 532 Leveraging Formal Methods and Fuzzing to Verify Security and Reliability Properties of Large-Scale High-Consequence Systems
- 534 Running Malware on Millions of Android Cell Phones
- 536 Geographically Distributed Graph Algorithms
- 538 Modeling and Development of Nondestructive Forensic Techniques for Manufacturer Attribution
- 539 Using Temporal Analysis for Robust Deception Detection

- 541 An Empirical Assessment of the Factors Underlying Phishing
- 542 Machine-Oriented Biometrics and Cocooning for Dynamic Network Defense
- 544 Flexible and Scalable Data Fusion using Proactive, Schema-Less Information Services
- 545 Training Cyber Situation Awareness in Blue Team Exercises

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- 550 AQUARIUS: Adiabatic Quantum Architectures in Ultracold Systems
- 551 Enabling Secure, Scalable Microgrids with High Penetration Renewables
- 552 Activity Based Intelligence, Data to Decisions
- 553 Science-Enabled Next Generation Photovoltaics for Disruptive Advances in Solar Power and Global Energy Safety and Security
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- 557 **Appendix A, FY 2012 Awards and Recognition**
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Sandia National Laboratories' FY 2012 Laboratory Directed Research and Development (LDRD) Program: *Discretionary Research and Development for the Future of the Labs*

Julia M. Phillips, Vice President and Chief Technology Officer



As authorized by Congress, the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories (Sandia) is essential to maintaining the vitality of our Labs in mission-critical science, technology, and engineering (ST&E) disciplines. As Sandia's sole discretionary R&D program, LDRD enables our technical staff to pursue creative, high-risk, and potentially high-impact research and development (R&D) that simultaneously enables Sandia's national security mission and advances the frontiers of science and engineering. Furthermore, LDRD-funded game-changing research leads to the development of the next generation of technical capabilities needed to address both established and emerging mission challenges. Innovation in LDRD projects is crucial to our overall mission of providing "exceptional service in the national interest."

All Sandia LDRD projects provide both direct and indirect benefit to the national security missions of the Laboratories and DOE/NNSA. LDRD is a key contributor to the development and use of science and engineering capabilities currently employed by the nuclear weapons program, such as fundamental and applied research in materials science to create MEMS-enabled integrated optical circuits, vapor-phase lubrication technology for advanced components, binary analysis tools for cyber-threat malware detection, new high-energy neutron spectrometers, and micro- and nanoelectronic advances for future quantum computing architectures. In addition, the LDRD program supports crosscutting R&D in nonproliferation, alternative energy sources, climate, infrastructure security, biothreat reduction, and cybersecurity, seeking ground-breaking technical solutions for some of the most challenging emerging ST&E issues facing our nation. LDRD projects often provide benefits to multiple missions, demonstrating an impact that is far broader than initially envisioned in the original proposal.

A robust peer-review process of proposals results in the selection of projects that are both of the highest technical quality and well-aligned with Sandia's national security missions. LDRD accomplishments are actively leveraged by management engaged with direct programs in order to maximize the impact of project results on national security.

The FY 2012 LDRD program supported 433 projects costing \$166 M. This annual report offers an overview of the LDRD projects that were ongoing in FY 2012, highlighting a few examples to demonstrate the broad scope of LDRD investments. The program overview and project summaries provide a window into the outstanding ST&E research conducted in the program as well as its potential for impact on national imperatives.

Sandia FY 2012 Program Overview

PROGRAM PURPOSE

With the current and future missions of the Department of Energy/National Nuclear Security Administration (DOE/NNSA) as our guiding principle, the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories (Sandia) supports our broad scope of national security missions in a forward-looking, proactive fashion. Per Congressional intent (P.L. 101-510) and DOE guidance (DOE Order 413.2B), Sandia's LDRD program is crucial to maintaining our scientific and technical vitality and enhancing our ability to address current and future national security missions. More explicitly, Sandia's goals for the LDRD program are as follows:

- Advance the frontiers of science and technology
- Enable innovative S&T in support of our national security missions

Within the LDRD program, Sandia staff have the opportunity to pursue leading-edge research ideas, hone their technical skills, develop their professional leadership, and advance the state of the art of science and engineering in support of the Labs' enduring national security missions.

With a budget of \$166 M for 433 projects in FY 2012, the program has underwritten myriad high-risk science, technology, and engineering (ST&E) projects, often in collaboration with scientists and engineers in academia, industry and other DOE laboratories. LDRD research has yielded outcomes contributing to nuclear, homeland, infrastructure, cyber, and energy security — in areas as diverse as novel sensor concepts and technologies, quantum science and technology, nanotechnology, metamaterials, computational modeling and simulation, carbon-neutral energy, molecular biology, and cognitive science. In turn, the results of this research support DOE missions in nuclear security, energy security, environmental responsibility, and scientific discovery and innovation, as well as broader national security missions of our WFO customers.

PROGRAM DESCRIPTION

PROGRAM ORGANIZATION AND STRUCTURE:

Responsibility for the Sandia LDRD program rests with the Sandia President, who delegates policy and process authority to the Chief Technology Officer (CTO). Reporting to the CTO, the LDRD Office is responsible for day-to-day program management, process development, final proposal review, monitoring of outcomes, reporting to the responsible NNSA entities, and when appropriate, conducting periodic operational program reviews for the purpose of recommending program and process amendments.

LDRD strategic investments are based on a balanced portfolio of major investment categories, called Program Areas (PAs), which generally consist of a few smaller more focused investment areas (IAs). The FY 2012 LDRD portfolio consists of five Program Areas: Mission Technologies (MT), Mission Challenges (MC), Science, Technology and Engineering Foundations (ST&E), Grand Challenges (GC) and Corporate Investments (CI).

PROGRAM AREA: Mission Technologies

The Mission Technologies Program Area seeks to create and nurture the ability to provide innovative future solutions for DOE and Work for Others (WFO) sponsors of the Laboratories' mission areas, creating or accelerating the development of the needed technologies for national security issues. The

four Mission Technologies IAs align with the Laboratories' Strategic Management Unit (SMU) structure:

- **Defense Systems and Applications (DSA):** Develop innovative, technology-based systems solutions to the most challenging issues facing the national security community.
- **Energy, Climate and Infrastructure Security (ECIS):** Develop and apply differentiating technologies in the areas of innovation for US energy security, climate change issues affecting national security, and infrastructure security.
- **International Homeland and Nuclear Security (IHNS):** Develop innovative solutions to lower the risk posed by nuclear and biological proliferation, terrorist threats, catastrophic incidents, and potentially destabilizing events.
- **Nuclear Weapons (NW):** Develop and create products and capabilities that incubate science, technology or engineering solutions for NW mission needs.

PROGRAM AREA: Mission Challenges

New in FY 2012, the Mission Challenges Program Area targets some of the most complex and difficult ST&E problems facing our nation that no one agency or industry can solve on its own, pursued key ST&E challenges spanning many years of R&D effort across multiple portfolios and disciplines, and created breakthroughs in science or engineering. In FY 2012, there was one Mission Challenge Investment Area:

- **Cyber Security (CS):** Establish, develop, and advance the scientific foundations for cyber security to enable much more robust approaches for addressing and mitigating the significant cyber vulnerabilities we face today and in the future.

PROGRAM AREA: Science, Technology, and Engineering Foundations

The Science, Technology, and Engineering Foundations Program Area seeks to anticipate and provide for the future ST&E needs of the Laboratory, fostering our science base as a means to further developing the critical existing and future ST&E capabilities that the SMUs need to support our national security missions. The five ST&E Foundations IAs are:

- **Enable Predictive Simulation (EPS):** Sponsor innovative research and development that revolutionizes the knowledge base and capabilities necessary for predictive simulation of complex problems.
- **Nanoscience to Microsystems (NTM):** Discover new phenomena at the nanoscale, and create or prove new concepts, materials, devices, processes, components, subsystems, and systems.
- **New Directions (ND):** Develop new competencies in the two thematic areas of biological science and technology, and cognitive science and technology.
- **Science of Extreme Environments (SEE):** Create new knowledge that enables revolutionary advances in the areas of high energy density physics, radiation sciences, pulsed power, and fusion energy for national security needs.

PROGRAM AREA: Corporate Investments

Corporate Investments support the strategic needs of Sandia as a national laboratory, nurturing our workforce, developing external partnerships, and seeking breakthrough science and technology.

- **Strategic Partnerships (SP):** Emphasizes research that supports the development of strategic academic partnerships, and/or targets strategic laboratory initiatives.
- **Early Career R&D (ECD):** Two-year-funded projects designed to assist new staff members in initiating research programs. Funds high-risk, potentially high-value research that enables the missions of Sandia, with a specific focus on the rapid integration of early career Ph.D. staff into the Sandia workforce.

PROGRAM AREA: Grand Challenges

Grand Challenges address some of the most difficult problems facing our nation, using larger (>\$2 M/year project) multidisciplinary teams to create significant ST&E advances that lead to unique or differentiated capabilities not likely to be duplicated elsewhere.

BUDGET:

The actual cost of the FY 2012 LDRD program was \$165.2 M of the \$166 M target budget. Figure 1 illustrates a breakdown of the FY 2012 portfolio by Program Area cost.

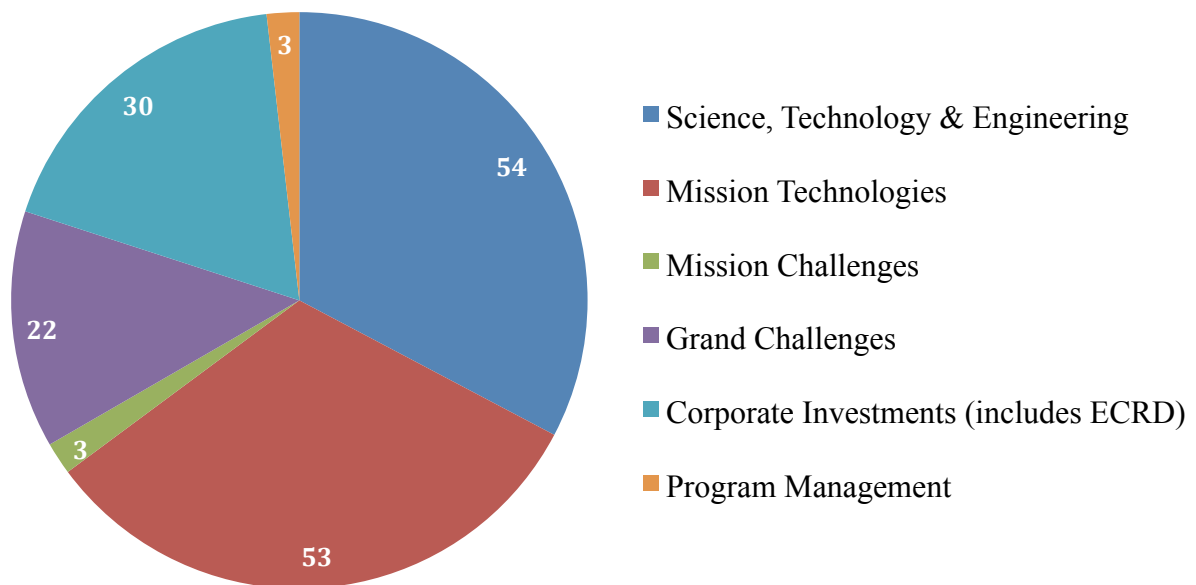


Figure 1: FY 2012 portfolio by Program Area cost (\$M)

FUNDING PROCESS:

Each Investment Area (IA) manager selects a small group of experienced managers and senior staff to manage their IA processes, including writing the call, reviewing proposals, and evaluating project progress. In addition, the IA team works with the principal investigator (PI) and project manager in leveraging project outcomes.

The process for selecting LDRD projects is a formal process described as follows:

- The Sandia Chief Technology Officer, in collaboration with the Executive Office, identifies the LDRD IA structure and budget targets.
- The Laboratories' LDRD Call for Ideas is written by the IAs, and describes the goals of the IAs, and their strategy to achieve those goals by addressing scientific and technical challenges through LDRD investments.
- Interested employees submit 500-word "ideas" online to the appropriate investment areas for evaluation. Grand Challenge ideas are twice the length of a normal idea.
- The IA teams scrutinize submitted ideas, seeking those that describe leading-edge R&D, have potential impact on future activities, and are aligned with Sandia's strategic missions.

- The IA then selects certain ideas from which to request full proposals for internal peer review. A proposal that details progress and tasks for the coming year is also needed for all continuation LDRDs. Proposal length varies with budget: at <\$2,000 K, a five-page proposal is written in addition to a proposal summary (data sheet); and for projects exceeding \$2,000 K (i.e., Grand Challenge), a 20-page proposal is submitted in addition to the proposal summary.
- Independent technical and programmatic appraisals are conducted on each new proposal. The IA teams then rank the proposals in order of funding preference, and select projects according to budget targets.
- Continuing projects submit an updated proposal summary (data sheet). These projects are reviewed annually (at a minimum) for technical progress and continued programmatic alignment.
- The LDRD office reviews and submits project summaries (i.e., data sheets) to the DOE/NNSA Sandia Site Office (SSO) for individual concurrence.
- The LDRD program office then prepares the annual program plan for review and approval by the Chief Technology Officer.

PROGRAM IMPROVEMENTS:

Sandia implemented a number of changes to the FY 2012 LDRD program, primarily in response to LDRD self-assessment activities that were conducted in FY 2011. These changes were primarily intended to increase transparency, the chief concern identified through participant surveys and focus group input.

Idea Review and Selection Process Changes

- PI name and organization number were removed from ideas sent to IAs.
- Selected ideas with title and PI name, and IA, were posted on the LDRD web site.

Proposal Review and Selection Process Changes

- New formats were implemented for both technical and programmatic reviews, to provide more substantive feedback and separate scoring.
- Names of IA team members and technical reviewers were posted on the LDRD web site.
- Proposal scores, names and titles were posted on the LDRD web site with selection decisions.
- The PI for every new proposal received an explanation for the IA's decision to fund or not fund.

With the exception of the anonymous idea submission, which resulted in several unintended consequences, these changes were well received by researchers, managers, and IA leaders, and will be continued.

PORTFOLIO DESCRIPTION:

For FY 2012, 811 ideas were submitted, from which 181 were invited to submit new (initial-funding) proposals, and 81 of these proposals were approved for funding, a final funding rate of 10%. To these were added 40 new Early Career R&D projects, and 25 other late starts, for a total of 146 new projects. These 146 newly funded projects were added to 287 continuing projects yielding a total of 433 LDRD projects funded for the fiscal year.

Mission Relevance:

LDRD projects are chosen for their technical quality, their differentiating and programmatic value to Sandia, and their relevance to DOE/NNSA's missions (nuclear security, energy security, environmental remediation, and scientific discovery and innovation), as well as the national security missions of the Department of Homeland Security, the Department of Defense, and Other Federal Agencies. As a result, the scientific advances and technology innovations from LDRD provide multiple benefits to all Sandia stakeholders, consistent with Congressional intent and our Laboratories' strategic goals. Figure 2 shows

the mission relevance of the FY 2012 LDRD portfolio, and in particular, the broad support for a suite of current and planned national security missions for that portfolio. The dollar amounts total more than 100 percent of the total FY 2012 budget since many projects impact and have relevance to more than one mission area.

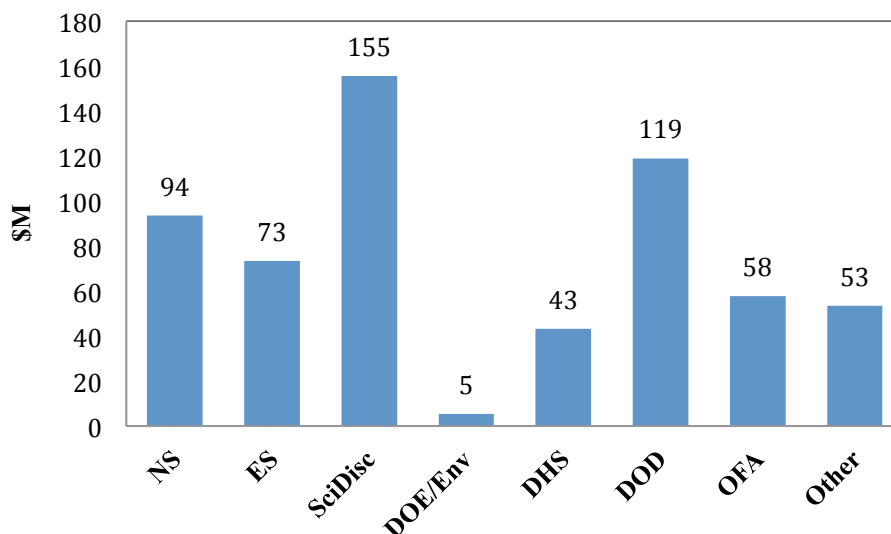


Figure 2. The FY 2012 LDRD portfolio supports multiple missions. DOE missions: Nuclear Security (NS), Energy Security (ES), Scientific Discovery (SciDisc), Environmental Responsibility (DOE/Env); and Department of Homeland Security (DHS), Department of Defense (DoD), Other Federal Agencies (OFA), and other organizations, e.g., industry (Other).

Project Size:

LDRD projects vary in size and scope. The FY 2012 project size, by budget, is shown in Figure 3.

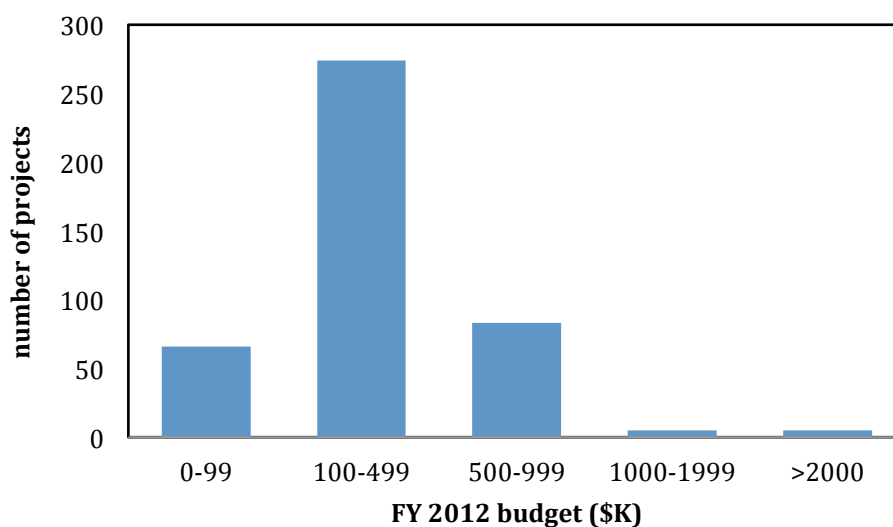


Figure 3. FY 2012 LDRD project size distribution, by budget

Project Strategic Intent Distribution:

The LDRD program supports a range of R&D activity from fundamental research through proof-of-principle studies and demonstrations. In this context, each project is accorded a strategic designation of Discover, Create, or Prove (D, C, or P). The intent of “Discover” projects is the creation of new understanding or knowledge. “Create” projects pursue the innovative application or combination of new or existing knowledge in a unique fashion, in order to create a novel solution to a problem, or to provide a revolutionary scientific, technological, or engineering advance. “Prove” projects pursue the validation of a prospective innovation or concept, in a fashion that reduces unknowns and uncertainties. The distribution of FY 2012 projects by DCP intent is shown in Figure 4.

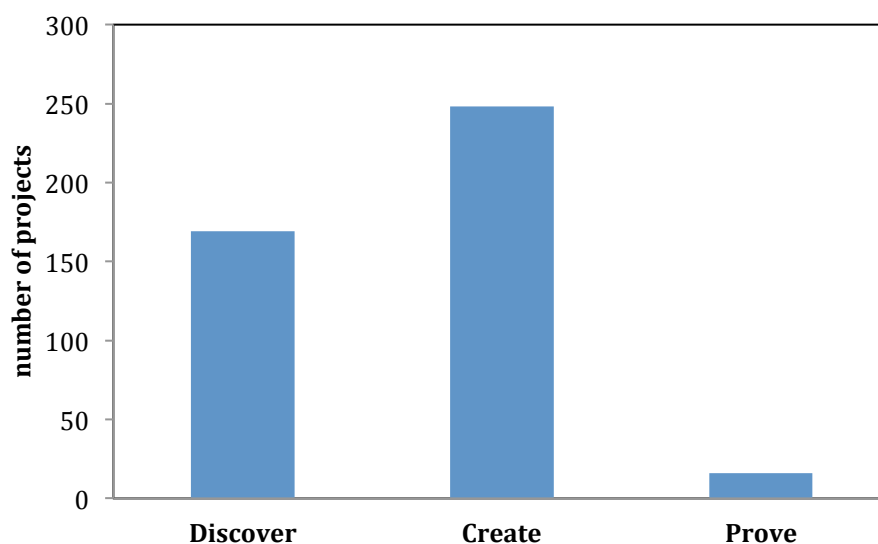


Figure 4. The DCP strategic intent distribution for the FY 2012 LDRD portfolio

EARLY CAREER R&D (ECRD):

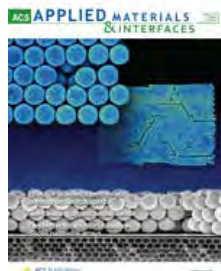
Initiated in FY 2010, the Early Career R&D (ECRD) element of the LDRD Program makes a maximum of \$500 K (\$250 K/yr) of LDRD funding available for a 24-month project, to Ph.D.-recipient technical staff members with less than one year on roll. ECRD is designed to enable a smooth transition of the new-hire into the Sandia workforce, allowing participants to focus on creative research activity, while simultaneously acclimating them to the national laboratory environment, with its dual focus on R&D and programmatic work. Originally open to all new Ph.D. level staff members, participants must now be selected according to a number of available slots allocated to the hiring organizations. In FY 2012, LDRD funded 40 new and 107 continuing ECRD projects. Two Early Career Days were held to feature program research outcomes, the first, a New Mexico–site poster session in August 2012, the second, a California-site poster session in early October 2012.

PROGRAM PERFORMANCE:

LDRD creates and builds new knowledge and novel technologies that develop new capabilities and produce major scientific advancements through leading edge R&D. Supporting evidence includes success stories and news coverage, awards and recognition, as well as statistical measures of outputs such as publications and intellectual property. In June of 2012, the LDRD Office published a brochure entitled, *LDRD Impacts on the Sandia Nuclear Weapons Program*. Additional examples are provided below.

SCHOLARLY PUBLICATIONS FEATURED ON JOURNAL COVERS

The impact of LDRD-funded research at Sandia is aptly illustrated by the recognition accorded Sandia scholarly publications deriving from LDRD research.



Capturing the cover of the August 2012 *Applied Materials & Interfaces*, this paper, “Effect of Ordered Intermediate Porosity on Ion Transport in Hierarchically Nanoporous Electrodes,” is backdropped by recent LDRD projects in the area of nanoporous electrodes.



“Solar Selective Coatings for Concentrating” in the January 2012 issue of the journal, *Advanced Materials & Processes*, describes thermal spray and other coatings for solar-concentrating mirror surfaces that increase the efficiency of reflected solar energy, maximizing solar thermal transfer to electricity-generating fluids while decreasing heat losses to the environment.

An invited article, “A Materials Investigation of a Phase-Change Micro-Valve for Greenhouse Gas Collection and other Potential Applications” made the March 2012 cover of the *American Institute of Physics Review of Scientific Instruments*. The described microscale technology for gas collection and storage has implications for monitoring of atmospheric greenhouse gases.



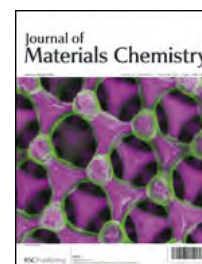
“Computational Aspects of Many-Body Potentials,” in the May 2012 issue of the *MRS Bulletin*, discusses the computational cost and power of molecular dynamics modeling for simulations that include many-body effects and large numbers of atoms.

“Orthogonal Cell-Based Biosensing: Fluorescent, Electrochemical, and Colorimetric Detection with Silica-Immobilized Cellular Communities Integrated with an ITO–Glass/Plastic Laminate Cartridge,” published in the September 2012 issue of *Small*, describes the use of living cells as sensors. Entrapped within a nanostructured silica matrix, the cells are engineered to produce a triple signal — fluorescent, electrochemical and colorimetric — in response to an analyte, thus conferring reliability and confidence in the sensor’s output. The cells remain viable for extended periods, and co-entrapment of both prokaryotic and eukaryotic cells was also achieved.



“Physiological Effects of Free Fatty Acid Production in Genetically Engineered *Synechococcus elongatus* PCC 7942,” the cover feature of the September 2012 issue of *Biotechnology and Bioengineering*, describes the genetic engineering of a cyanobacterium (prokaryotic alga) to produce greater quantities of the biodiesel precursor free fatty acids desirable for enhanced biofuels production together with this engineering’s effect on energy metabolism and cell growth.

Initially published in September 2012, this work, entitled “Three Dimensional Nickel–Graphene Core-Shell Electrodes,” published in the *Journal of Materials Chemistry*, described a method for creating an intriguing core-shell electrode, with a nickel core encapsulated by a 3D graphene shell. Initially coating more-random sp^3 -bonded carbon with nickel, the researchers discovered a way to graphitize the structure, the carbon converting to largely sp^2 -bonded 3D graphene. Simultaneously with this transition, the nickel-coated 3D graphene transformed to nickel-encapsulated graphene as the two elements changed position by apparently diffusing through each other.



2012 AWARDS AND RECOGNITION:

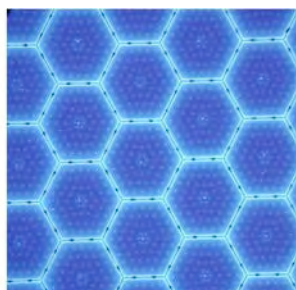
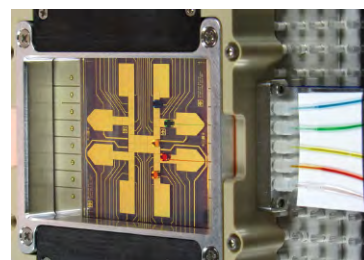
In 2012, Sandia received four R&D100 Awards, all of which had their roots in LDRD projects.

1. In the area of neutron generation for applications as diverse as energy exploration and medical therapeutics, the *Neutristor* — a product of clever design and engineering — offers a solid-state, ultraminiaturized neutron generator.



2. *The Sandia Cooler* is a fundamental redesign of heat exchangers that can greatly increase the efficiency of heat dissipation for applications in central processing unit cooling, as well as for air conditioning. Approximately 30 times more efficient than conventional air-cooled exchangers, it is also quiet and defeats the problem of dust-and-debris fouling that plagues conventional heat exchangers.

3. *The Digital Microfluidics Hub* forms a microfluidics control/routing module for efficient, programmable microdroplet-based reagent trafficking in microscale analytical chemistry, particularly as applied to biological specimens, such as nucleic acid hybridization.



4. *Miniaturized Photovoltaics* revolutionizes solar photovoltaic cells by creating cells of approximately 250- μm diameter and approximately 15 μm thick, which exhibit efficiencies greater than 12% with possible expected efficiencies as high as 40%, and which can be conformally molded to irregular surfaces.

Gregory Nielson, the principal investigator (PI) on the fourth R&D100 winner — based on a project entitled *Science-Enabled Next Generation Photovoltaics for Disruptive Advances in Solar Power and Global Energy Safety and Security* — was named by *Popular Science* Magazine as one of its “Brilliant 10,” one of the ten scientists most likely to positively impact the nation’s science and engineering innovations.

In addition, other LDRD participants have been recognized for notable technical achievements through awards from professional societies and organizations, as included in Appendix A. These awards,

together with the journal covers and the R&D100 awards as just described, delineate a pattern of LDRD-project impact on the broader ST&E community, supporting the view that LDRD projects serve the dual role of both supporting the missions of Sandia and DOE/NNSA and also contributing to the leading edge of science and engineering knowledge.

EXTERNAL REVIEW OF SANDIA'S LDRD PROGRAM:

In FY 2012, for the first time, the Sandia Research Advisory Board (SRAB), including the chairs of each of the Research Foundation External Review Boards (ERBs), performed a comprehensive external review of the LDRD program based upon an integration of the individual ERB reviews and External Advisory Board (EAB) reports for our Grand Challenge projects. The SRAB report is generally very favorable, and includes some recommendations that will influence future LDRD program investments and processes. The SRAB report stated that the LDRD program exhibits very high quality research that is relevant and well aligned with Sandia's missions. Finally the SRAB noted that many of Sandia's successes could be traced back to investments in LDRD.

ENABLE PREDICTIVE SIMULATION INVESTMENT AREA

Computational modeling and simulation is the bailiwick of this investment area (IA), funding research into computational activity that has the capability to both confirm and globalize experimental results, as well as to guide future experimentation and scientific intervention into national and global challenges. From models of material failure probabilities and explosive dynamics, to modeling water systems in semi-arid regions, to clarifying the properties of matter at the nanoscale, to new designs for computational memory, this IA's reach across Sandia's mission areas is quite extensive.

Multiscale Models of Nuclear Waste Reprocessing: from the Mesoscale to the Plant Scale Project 141508

This project has developed a PUREX model in SIERRA Mechanics, Sandia's high performance computing multiphysics code suite and Cantera, an open source software product for thermodynamics and kinetic modeling. It included experiments at the droplet and contactor-scales and focused on modeling at these scales. Advanced thermodynamic methods in Cantera for uranyl transport from acid solution to the organic phase can predict distribution coefficients for various acid and tributyl phosphate concentrations. Novel centrifugal contactor experiments with quantitative measurement of 3 phases, water, organic drops, and air bubbles have been developed. Microfluidic experiments were also developed enabling the understanding of droplet-formation and internal flows for an aqueous-organic system. A non-radioactive model system together with a new spectrophotometer provides quantitative mass transport data for the validation study. This system is used to study mass transport in both the droplet-scale microfluidic experiments and for contactor-scale experiments. A novel population balance kernel for drop breakup has also been developed.



Contactor-scale experiment and simulation of turbulent flow in a contactor using Sierra Mechanics

Effects of Morphology on Ion Transport in Ionomers for Energy Storage Project 141506

Ionomers are largely nonpolar copolymers that contain a small percentage of ionic groups. Although various material science applications have been suggested for this class of substance, a leading application of interest to DOE is the possibility of using ionomers as alternative battery electrolytes. Problematically, in both aqueous and organic-solvent liquid electrolytes, packaging in batteries poses a difficult and quite expensive challenge. Even further, liquid electrolytes are frequently corrosive or flammable. Additionally, certain charge-transfer issues can limit their effectiveness. Hence, chemists have been seeking alternatives to this wet chemistry that do not contain aqueous or organic solvent ion solutions, but still supply balancing ionic currents with adequate conductivity. Ionomers are under consideration for this role.

In this molecular dynamics research, the team modeled representations of ionomer melts. The ionic groups were placed in various configurations along the polymer backbone (for example, periodic and random) in order to shed light on the mechanism by which charge transfer occurs. Tandem experimental work using x-ray scattering has validated the modeling approach as having realistic connections to the actual chemistry. The project also performed quantum density functional theory (DFT) calculations of structures and energies of several ions (Li, Na, Cs, and Zn). The research has assessed the effect of ionomer structure on conductivity, and to clarify the mechanism of charge transfer within ionomer melts.

Prior research had strongly suggested that movement of charge in ionomer melts occurs by a “hopping” mechanism. The current Sandia research suggests a different mechanism: during this aggregation of ionic groups, the ionic groups move by cluster collisions and rearrangements rather than by “hopping” between clusters, almost as though the ions are “handed-off” and pushed through the medium by these molecular rearrangements, thus accounting for the charge conductivity properties of the ionomer melt.



Model of interaction of ionic sites in ionomers.

This alternative explanation for ion conductivity could suggest different routes forward toward sufficiently improving conductivity of ionomer melts to make them viable as battery electrolytes.

Enable Predictive Simulation Investment Area

An Internet Emulation System to Enable Predictive Simulation of Nation-Scale Internet Behavior 141505

Year 3 of 3

Principal Investigator: R. C. Armstrong

Project Purpose:

We are engaged in a three-year project to address one of the hardest problems confronting the US: the near-continuous set of attacks that afflict government institutions, businesses, and individuals. These attacks are usually managed by software known as botnets. Botnets are autonomous, stealthy, and can cause great damage, pulling data from an organization and distributing it to organized criminal organizations or, possibly, nation states. As this is written, Sony's Play Station Network has been shut down, affecting over 75 million users worldwide, with unknown long-term consequences.

Today's popular information technology (IT) solutions, such as virus detectors, are known to be near useless, as John Chambers, chairman of Cisco, and a recent JASONS report have both pointed out. In fact, there is little software available today that is of any use at all: datalossdb.org shows a near-constant loss of data, month by month, even as vendors scramble to patch software, close firewalls, and set up policy and procedures that they hope will help. One might think by reading the statistics that no one had put any effort into data protection in the last 30 years — that illustrates how ineffective our measures have been.

This project aims to make botnet and other malware detection automatic. To do so, we must stand up a real botnet in an isolated way. We accomplish this by applying high performance computing techniques to the problem of running hundreds of thousands of Windows or millions of Linux images, using virtual machine technology. By running these “virtual machines,” we can run a real botnet and understand its behavior. Once the behavior is understood, we can consider defenses that work, and test those defenses on our virtual machine system. No other group has come even close to achieving such a large and accurate simulation.

Summary of Accomplishments:

This year, we hardened, documented, and simplified the interface so that the community at large could use it. It is not exactly a turnkey system but it is much closer than last year. Megatux is in active use by multiple federal agencies.

Significance:

Emulating nation-scale networks is of great use in the cyber and IO communities for numerous federal agencies, from DOE to DoD and DHS.

Effects of Morphology on Ion Transport in Ionomers for Energy Storage 141506

Year 3 of 3

Principal Investigator: A. Frischknecht

Project Purpose:

Polymer electrolytes are essential elements of current and next-generation energy storage applications. An important class of polymer electrolytes is ionomers, in which one of the ions is covalently bound to the polymer backbone. Ionomers are currently used in fuel cells, and show extraordinary promise as solid electrolytes in batteries for transportation and portable-power applications. Solid electrolytes are desirable for a variety of reasons. A primary one is safety: the lack of solvent leads to fewer electrochemical reactions (e.g., with the electrodes) and the absence of flammable liquids. Solvent-free electrolytes allow for less packaging (and hence higher energy density batteries) and easier manufacture. Single-ion conductors such as ionomers also have the advantage of higher efficiency (high lithium transference numbers), since the anions are bound to the polymer backbone and the current is primarily due to the cations that actively participate in the electrochemical reactions. However, to date, ionomeric materials do not have sufficiently high conductivities. Ion transport mechanisms in ionomers and their relation to molecular structure are poorly understood, although it is known that ion transport is coupled to polymeric motion and to the nanoscale morphology of ionic aggregates that often self-assemble in the polymer matrix. We are developing and using a suite of multiscale models and tools to investigate the structure of ionic groups and aggregates in ionomers and to predict their effects on ion transport. The ability to predictively model these materials will enable the design and synthesis of new ionomers, which could lead to sizeable improvements in battery safety and performance essential for electrified vehicles.

This project is focused on the challenging tasks of developing the modeling tools necessary to treat charged polymeric systems and using those tools to understand the fundamental mechanisms that control ion transport in polymer electrolytes.

Summary of Accomplishments:

In this project, we focused on understanding a model set of poly(ethylene-co-acrylic acid) (PE-AA) ionomers, using both molecular simulations and experiments. We performed a large set of coarse-grained (CG) molecular dynamics (MD) simulations of ionomer melts with varying architectures, and a second large set of atomistic MD simulations of PE-AA ionomers, both in the acid form and neutralized with Li, Na, Cs, and Zn ions. Both sets of MD simulations showed that the ionic aggregates have a wide variety of shapes, depending on the polymer architecture and cation. The scattering structure factors from both CG and atomistic simulations are in good agreement with x-ray scattering data. In the CG simulations, the counterions were found to diffuse faster in the systems with extended, percolated aggregates, suggesting that percolated aggregates are better for high conductivity. The mechanism for counterion motion is one of cluster rearrangement, rather than ion hopping. We also performed quantum density functional theory (DFT) calculations of structures and energies of ions (Li, Na, Cs, and Zn) interacting with acetate molecules (to mimic a fragment of the ionomer). We find the optimal number of ligands for the monovalent ions is two forming a bidentate structure. For the divalent ions, the optimal number is three forming a six-fold coordinated ion. Experimentally, the PE-AA ionomers have been characterized with ^1H , ^{13}C , and ^7Li NMR (nuclear magnetic resonance spectroscopy). We found the acid form of the polymer forms strong dimers, while details of molecular architecture and neutralization level affect the morphology of amorphous and crystalline regions in the various systems. The Li NMR revealed two different Li environments, which were rationalized by comparison with our

atomistic MD simulations. Finally, we synthesized large quantities of PE-AA copolymers for use in future experiments.

Significance:

Improved electrical energy storage is crucial to the energy future of the nation. This project contributes to DOE's mission in energy storage by enabling predictive simulation of a potentially revolutionary new ionomer electrolyte. In this project, we demonstrated the feasibility of simulating ionomer melts and changed the prevailing scientific view of the molecular details of ionic aggregation in these systems. We advanced understanding of how polymer architecture affects ionic conductivity, necessary to designing future better electrolytes.

Refereed Communications:

L.M. Hall, M.J. Stevens, and A.L. Frischknecht, "Dynamics of Model Ionomer Melts of Various Architectures," *Macromolecules*, vol. 45, pp. 8097-8108, October 2012.

J.E. Jenkins, M.E. Seitz, C.F. Buitrago, K.I. Winey, K.L. Opper, T.W. Baughman, K.B. Wagener, and T.M. Alam, "The Impact of Zinc Neutralization on the Structure and Dynamics of Precise Polyethylene Acrylic Acid Ionomers: A Solid-State ^{13}C NMR Study," *Polymer*, vol. 53, pp. 3917-3927, August 2012.

L.M. Hall, M.E. Seitz, K.I. Winey, K.L. Opper, K.B. Wagener, M.J. Stevens, and A.L. Frischknecht, "Ionic Aggregate Structure in Ionomer Melts: Effect of Molecular Architecture on Aggregates and the Ionomer Peak," *Journal of the American Chemical Society*, vol. 134, pp. 574-587, December 2011.

T.M. Alam, J.E. Jenkins, D.S. Bolintineanu, M.J. Stevens, A.L. Frischknecht, C.F. Buitrago, K.I. Winey, K.L. Opper, and K.B. Wagener, "Heterogeneous Coordination Environments in Lithium-Neutralized Ionomers Identified Using ^1H and ^7Li MAS NMR," *Materials*, vol. 5, pp. 1508-1527, August 2012.

Multiscale Models of Nuclear Waste Reprocessing: from the Mesoscale to the Plant Scale

141508

Year 3 of 3

Principal Investigator: R. R. Rao

Project Purpose:

Nuclear waste reprocessing and nonproliferation models are needed to support the renaissance in nuclear energy, a proven technology without a carbon footprint. Our aim is to develop predictive capabilities targeting the design and monitoring of a next-generation nuclear fuel cycle to enable economic large-scale reprocessing with accurate material balances to mitigate public concerns regarding waste disposal and proliferation. The goal of this project was to develop a PUREX model in SIERRA Mechanics, Sandia's high performance computing multiphysics code suite and Cantera, an open source software product for thermodynamics and kinetic modeling. Originally we sought to develop modeling capabilities from the plant scale to the droplet scale. Unfortunately, our work to develop models at the plant-scale leveraged a DOE Advanced Scientific Computing Research (ASCR) project to develop a novel, scalable network model to be used to create processing plant "flow sheets." We redirected our work to include more experiments at the droplet and contactor-scales and shifted the focus to modeling at these scales.

Much of the focus of the project has been to develop a moving conformal decomposition finite element method (CDFEM) method applicable to mass transport at the water/oil droplet interface that occurs in the turbulent emulsion of droplets within the contactor. Models were developed contactor-scale using SIERRA Mechanics turbulence modeling capability with the classic level-set method. Unit operations occur at the column-scale where many contactors are connected in series. Population balances models were developed to investigate placements and coupling of contactors at this scale. Thermodynamics models of the PUREX separation were developed in Cantera to allow for the prediction of distribution coefficients for variation concentrations of surfactant and acid.

Summary of Accomplishments:

We have made improvements to SIERRA Mechanics, the engineering production code for the complex, for solid-fluid interactions and multiphase flows using our novel moving boundary algorithm termed conformal decomposition finite element method (CDFEM). We have developed advanced thermodynamic methods in Cantera for uranyl transport from acid solution to the organic phase, which can predict distribution coefficients for various acid and tributyl phosphate concentrations. Novel centrifugal contactor experiments with quantitative measurement of 3 phases, water, organic drops, and air bubbles have been developed. We have developed microfluidic experiments to understand droplet-formation and internal flows for an aqueous-organic system. We have developed a non-radioactive model system, based on neodymium and xylenol orange, with a new spectrophotometer to give quantitative mass transport data for the validation study. This system is used to study mass transport in both the droplet-scale microfluidic experiments and for contactor-scale experiments. A novel population balance kernel for drop break up has been developed.

Significance:

We have developed and implemented novel computational methods in SIERRA Mechanics our production engineering code. A new thermodynamics framework for separations was developed in Cantera. We have new experimental capabilities for microfluidics and separations. We have made scientific contributions to the literature and created environments for collaboration and advancements in conformal finite decomposition for moving boundary problems through our mini-symposia organization.

The Sandia and NNSA nuclear weapons (NW) mission will benefit with new computational methods to help understand manufacturing processes, performance, and abnormal environments. Some NW applications that will benefit from this work include foam manufacturing, explosive property prediction, melting/decomposition in abnormal environments, and thermal batteries performance.

Refereed Communications:

C.F. Jove-Colon, H.K. Moffat, and R.R. Rao, “Thermodynamic Modeling of Liquid-Liquid Extraction,” to be published in *Solvent Extraction and Ion Exchange*.

M.B. Nemer, P. Santoro, X. Chen, J.B. Blawdziewicz, and M. Loewenberg, “Coalescence of Drops with Mobile Interfaces in a Quiescent Fluid,” to be published in the *Journal of Fluid Mechanics*.

R.R. Rao, L.A. Mondy, T.A. Baer, D.R. Noble, C. F. Brooks, and M.M. Hopkins, “3D Numerical Modeling of Mold Filling,” invited eBook chapter in *Numerical Modeling*, InTech - Open Access Publisher.

J.B. Lechman, M.B. Nemer, and D.R. Noble, “Toward Application of Conformal Decomposition Finite Elements to Particle Suspensions,” *International Journal for Numerical Methods in Fluids*, vol. 68, pp. 1409–1421, April 2012.

C.C. Roberts, R.R. Rao, M. Loewenberg, C.F. Brooks, P. Galambos, A.M. Grillet, and M.B. Nemer, “Comparison of Monodisperse Droplet Generation from a Flow-Focusing Device with Hydrophilic or Hydrophobic Surfaces,” *Lab on a Chip*, vol. 12, pp. 1540-1547, April 2012.

R.R. Rao, T.A. Baer, and D.R. Noble, “Computational Fluid Mechanics for Free and Moving Boundary Problems,” *International Journal for Numerical Methods in Fluids*, vol. 68, pp. 1341–1342, April 2012.

Predictive Multiscale Modeling of Thermal Abuse in Transportation Batteries 141509

Year 3 of 3

Principal Investigator: R. P. Muller

Project Purpose:

Transition from fossil-fueled to electrified vehicles depends on developing economical, reliable batteries with high energy densities and long life. Safety, preventing premature or catastrophic failure, is of paramount importance in battery design. The largest gaps in our technical understanding of the safe operation of electrical energy storage devices involve the fundamental mechanisms, energetics, and inefficiencies of complex processes that occur during battery operation that can lead to thermal runaway: charge transfer, charge carrier and ion transport, both in the bulk and at various interfaces, and morphological and phase transitions associated with Li-ion transport between cathode and anode. We will develop a comprehensive predictive capability for thermal management and the onset of thermal runaway in transportation-based secondary Li-ion batteries, rooted in a first-principles description of the governing atomistic processes at the electrode-electrolyte interface, propagating chemical information through multiple scales to a continuum-scale description of thermal transport and failure capable of addressing a variety of operational and thermal excursion conditions.

Summary of Accomplishments:

We developed a multiscale modeling toolkit for determining the chemical mechanisms related to battery safety degradation and applying them to larger scale phenomena such as passivation layer degradation at the mesoscale, and cell performance at the macroscale. A number of the individual tools we have developed are notable, including an electrode-electrolyte simulation capability, and a phase-field modeling capability to describe passivation formation and degradation.

Significance:

We have explored and advanced multiscale modeling capabilities in this project, which are central to many aspects of Sandia's mission. We have built our software atop much of the scalable capabilities developed for the nuclear weapon stockpile, and in so doing, have verified the utility of this code. The development of such a comprehensive model will enable scientists and engineers to identify and address potential safety and stability issues of new battery designs prior to experimental realization. This will constitute a unique capability and will be of great significance within Sandia, for the DOE and DoD, and for its current and future commercial partners.

Refereed Communications:

R. Spotnitz and R. Muller, "Simulation of Abuse Behavior of Lithium-Ion Batteries," *Electrochemical Society Interface*, vol. 21, pp. 57-60, 2012.

J. Deng, G.J. Wagner, and R.P. Muller, "Phase Field Model of Solid Electrolyte Interphase Formation in Li-ion Batteries," *MRS Proceedings*, vol.1440, 2012.

Risk Assessment of Climate Systems for National Security 141510

Year 3 of 3

Principal Investigator: G. A. Backus

Project Purpose:

The US executive branch, many members of Congress, and defense and intelligence communities recognize that climate change has considerable potential to create high-consequence security threats. They further recognize the gap between climate science and Sandia's engineering risk-based analyses needed to characterize the national security threat. National security issues arising from perceptions of climate change already produce geopolitical tensions within the Arctic, Russia, China, and Africa. From population migration, to the loss of economic viability, to the new access to critical resources, to the disruption of strategic supply chains, climate change produces destabilization hazards across countries. To understand geopolitical issues, we must understand the dynamics of regional climate change and its concomitant effects on human and state behavior. Moreover, we must understand and accommodate the inescapable uncertainty in physical and human-behavioral modeling before we can assign any level of confidence (validation) to the results that analyses produce. This effort will extend our existing climate capabilities to perform regional analyses and a comprehensive characterization of potential security threats. We are identifying emergent and signpost phenomena of climate change, along with sensitivity fingerprints. We are coupling climate change, hydrological and socioeconomic analyses with new uncertainty quantification methods (adapted from Sandia's Advanced Scientific Computing [ASC] and new Office of Science [SC] work) for examining the high-consequence tails of the climate probability distributions that dominate the risks and impacts for societies and economies. Our previous work established that the primary path of climate change risk follows a course from local hydrological impacts affecting the ability to maintain local economic activity. Interregional socioeconomic interactions then produce ripple-effect impacts on a global scale with geopolitical ramifications. Decision support systems to quantify and manage the associated risk thereby require multiscale and coupled analyses. Methods to measure and encapsulate the dynamic uncertainty for supporting risk-informed policymaking are non-existent.

Summary of Accomplishments:

We developed new methods to evaluate the tail region of probabilistic results from computationally intense climate models and new methods for management confidence for socioeconomic and behavioral models. We evaluated the current preferred models for land-use and hydrological impacts, and rejected it because it could not realistically address the impact on humans. We then worked with the University of Illinois to modify a global hydrological model that could address climate induced, hydrological impacts on humans. We developed new methods to determine cloud formation and aerosol impact. We demonstrated emergent phenomena in the future Arctic and evaluated the impact of reduced ice-cover on economic and national security issues. We developed new methods to address the impact of climate change on infrastructure and were given four lead-authorships for the White House directed 2013 National Climate Assessment.

Significance:

Climate change impacts potentially affect numerous aspects of DOE and DHS missions, from energy production and electric grid functioning through such DHS interests as port operation and security. Our work stands to contribute to the understanding of climate change phenomena.

Refereed Communications:

S. Nash, “Human Impacts of Climate Change,” invited book for University of Virginia Press, (interviews and work of M. Boslough, M. Taylor, and G. Backus).

H. Schmidt, A.R. Kerstein, R. Nédélec, S. Wunsch, and B.J. Sayler, “Numerical Study of Radiatively Induced Entrainment,” *Journal of Physics: Conference Series*, vol. 318, section 7, 2011.

G.A. Backus, T.S. Lowry, and D.E. Warren, “The Near-Term Risk of Climate Uncertainty among the US States,” *Climatic Change*, vol. 116, pp. 495-522, February 2013.

Streaming Data Analysis for Cybersecurity 141511

Year 3 of 3

Principal Investigator: S. J. Plimpton

Project Purpose:

A ubiquitous task in cybersecurity is monitoring network traffic, looking for anomalies that indicate incoming attacks, intruders or malware already inside a local network, or data exfiltration. Monitoring typically involves data collection and post-processing of archived log files using manually updated filters along with human inspection and judgment. While effective, this approach has limitations: timely responses may be impossible, analyses may be inaccurate or incomplete since data exceeds storage capabilities, and rapidly evolving attack strategies may be undetectable.

These issues can potentially be addressed by modeling and analyzing the stream of network traffic in real time, as it is captured. We are devising and implementing new streaming algorithms to overcome these challenges and enable the power of post-processing methods, which employ graph-based algorithms and classification techniques, to be applied in real time. We are focusing on two cyber problems of critical importance to Sandia: malware and botnet detection. The former involves not only the classification of downloaded software, but also characterization of the preceding events and bad sites that enabled it. The latter involves detection of machines inside our network that communicate inappropriately, are under external control, or which exfiltrate their files.

We are validating our algorithms using the rich compendium of archived “event” data that Sandia has and will continue to collect. If successful, we anticipate our software will be used in Sandia monitoring efforts, and at other government agencies.

Streaming analysis and algorithms are challenging in several respects. They operate in real time on large volumes of input data, they are constrained in their memory usage and computational cost, and they must age (expire) data appropriately. Developing graph and classification techniques that work effectively in this mode is a new and growing area of algorithms research, with application not only to cybersecurity, but also to data mining and informatics more broadly.

Summary of Accomplishments:

The focus of this project was to develop new algorithms and methodologies for computing on streaming data that arrives in real time, with an emphasis on streaming network data for cybersecurity applications. We highlight four specific accomplishments:

1. We have designed and deployed two data collection pipelines, one in New Mexico and one in California. These continuously collect WWW traffic and downloaded EXE and PDF files and archive the information into two fast no-structured query language (SQL) databases. The databases also support real-time back-end processing, whereby we wrote additional tools to analyze the data in near-real time and flag suspicious events for cyber analysts (e.g., in the form of daily reports).
2. We have applied machine-learning methods using ensembles of streaming decision trees to analyze and classify downloaded EXE files as goodware versus malware. This uses either static or dynamic properties of the files, the latter via running them in the server cluster FARM sandbox system for a few minutes. The trees were enhanced to make them more robust to “concept drift,” where the malware properties change over time.

3. We wrote an open-source framework called PHISH for developing and running streaming algorithms in parallel on distributed-memory platforms. It can be downloaded from <http://www.sandia.gov/~sjplimp/phish.html>. We used PHISH to write two parallel graph algorithms that find triangles and sub-graph isomorphism matches in an incoming stream of edges.
4. We invented a new streaming graph algorithm for finding connected components in parallel. Its data structures and operations have the unique property of only requiring constant-time work per incoming edge, so it is guaranteed to keep up with streams up to a certain data rate. It can also answer real-time queries about the graph and its components.

Significance:

The malware detection capability will be deployed by cyber analysts in California. Discussions with New Mexico analysts are ongoing. The data collection pipelines will continue to be used by other projects at Sandia. The streaming graph algorithm work is being published in the open literature. The availability of PHISH as open-source software may lead to new collaborations with external or internal partners. Moreover customers such as DoD and DHS can readily benefit from this software.

Refereed Communications:

S.A. Mitchell, "Geometric Comparison of Popular Mixture Model Distances," to be published in the *Journal of Modern Mathematics Frontier*.

Understanding the Fundamentals of Plastic Deformation 141712

Year 3 of 3

Principal Investigator: C. R. Weinberger

Project Purpose:

This project looks into a few fundamental aspects of plasticity at the micro- and nanoscale: dislocation motion and multiplication, dislocation nucleation, and homogenization of dislocation structures.

Dislocation motion in small volumes is complicated because of the high surface-to-volume ratio in these structures. Much of the research has so far concentrated on how the free surfaces give rise to additional forces and the annihilation of dislocations at the surface. However, additional effects of free surfaces are less well known.

The nucleation of dislocations from free surfaces, which is important in nanomechanics, depends on a variety of factors including loading direction, surface orientation and the surface topology. The strength of nanomaterials is controlled by dislocation nucleation from surfaces and therefore models of this are greatly needed. Furthermore, there is a lack of comparisons with the emerging experimental evidence, which is naturally more complicated.

Homogenization of dislocation structures is difficult because it is unknown how the overlying mechanical properties are connected to material microstructure, which may also depend on the loading conditions. This project aims at identifying important variables that describe the dislocation structure evolution using dislocation dynamics, which can help predict mechanical properties.

The PI is a Harry S. Truman Fellow.

Summary of Accomplishments:

We developed a continuum model for dislocation nucleation from free surfaces based on atomistic inputs. The continuum model is able to describe multiple materials (gold, silver, copper, aluminum, and nickel) for a variety of orientations ($\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$). This model was used to predict the transition from single arm source operation to heterogeneous nucleation as a function of material and crystallographic orientation.

We have also investigated the behavior of single arm sources in nanopillars using molecular dynamics. We discovered that these sources are generally unstable (ephemeral) at these scales; the dislocations easily escape to the free surface. We also showed that we can artificially pin dislocations in these small volumes, which allow us to study their behavior. Our simulations showed that the pinned dislocations behave as Frank-Read sources with the appropriate strength and dynamics.

The mechanical properties of bicrystalline nanowires were also investigated using molecular dynamics. These simulations show promise as a way to investigate how dislocations interact with grain boundaries. Notably, we see that symmetric tilt grain boundaries do not emit dislocations as readily as random high-angle grain boundaries, suggesting that they act more as a sink to lattice dislocations while the random high-angle grain boundaries act as both a sink and source to dislocations.

Significance:

Sandia's success relies on being at the forefront of materials characterization, modeling and development. The research will provide improved fundamental basis for the development of materials

models for the full range of programs at the laboratories. Specifically, it addresses the problems of modeling material mechanical properties at the small scale and these developments are important for interpreting small-scale mechanical measurements and comparisons. These properties are of potential importance to multiple DOE alternative-energy initiatives, for example, superior LED development.

Refereed Communications:

C.R. Weinberger, C.C. Battaile, T.E. Buchheit, and E.A. Holm, "Incorporating Atomistic Data of Lattice Friction into BCC Crystal Plasticity Models," *International Journal of Plasticity*, vol. 37, pp. 6-30, October 2012.

A.T. Jennings, C. Gross, F. Greer, Z.H. Aitken, S.-W. Lee, C.R. Weinberger, and J.R. Greer, "Higher Compressive Strengths and the Bauschinger Effect in Conformally Passivated Copper Nanopillars," *Acta Materialia*, vol. 60, pp. 3444-3455, May 2012.

C.C. Battaile, B.L. Boyce, C.R. Weinberger, S.V. Prasad, J.R. Michael, and B.G. Clark, "The Hardness and Strength of Metal Tribofilms: An Apparent Contradiction between Nanoindentation and Pillar Compression," *Acta Materialia*, vol. 60, pp. 1712-1720, February 2012.

C.R. Weinberger and G. J. Tucker, "Atomistic Simulations of Dislocation Pinning Points in Pure Face-Centered-Cubic Nanopillars," *Modeling and Simulation in Materials Science and Engineering*, vol. 20, p. 075001, 2012.

C.R. Weinberger and W. Cai, "Plasticity of Metal Nanowires," *Journal of Materials Chemistry*, vol. 22, pp. 3277-3292, January 2012.

C.R. Weinberger, A.T. Jennings, K. Kang, and J.R. Greer, "Atomistic Simulations and Continuum Modeling of Dislocation Nucleation and Strength in Gold Nanowires," *Journal of the Mechanics and Physics of Solids*, vol. 60, pp. 84-103, January 2012.

Advanced Constitutive Models for Thermally Activated Shape Memory Polymers: Connecting Structure to Function

146013

Year 3 of 3

Principal Investigator: J. A. Zimmerman

Project Purpose:

Thermally activated shape memory polymers (SMP) can be manufactured to memorize a permanent shape, programmed thermomechanically to hold a temporary shape, then deployed back to its permanent shape in response to a specific temperature event. Compared to shape memory alloys, SMPs are inexpensive to manufacture. They are malleable and damage tolerant, and can undergo large, controllable shape changes in excess of 100% strain. SMPs are being investigated for a variety of applications, including temperature sensors, deployable and morphing structures for aerospace and biomedical. The shape memory performance depends on the complex interactions of many microstructural and thermomechanical factors, and considerable opportunities exist to tailor the polymer structure and the thermomechanical programming procedure to achieve the desired shape memory performance.

Our work initially focused on type I SMPs described by covalently cross-linked amorphous networks. The shape memory effect is provided by the equilibrium configuration of the cross-linked network. Shape storage and recovery is achieved by the glass transition and is strongly influenced by viscoelastic relaxation. While the thermo-mechanical properties of SMPs are highly customizable, the connections between thermomechanical properties and shape memory performance are unclear. Our goal is to develop advanced constitutive models for SMPs to study the connection between polymer structure, thermomechanical properties, and shape memory performance.

Summary of Accomplishments:

We have developed a coupled thermoviscoelastic model for amorphous polymer networks. The model combines the effects of broad stress and structural relaxation spectrum above the glass transition temperature (T_g), yielding and post-yield softening below T_g , and heat conduction. In addition, we focused our efforts in FY 2012 on studying the solvent driven shape memory effects and environmental aging in amorphous polymers. We developed formulations for a random copolymer network, which allow for independent tailoring of the glass transition, rubbery modulus, and swelling ratio for water. The system uses two different monomers, methyl acrylate (MA), methyl methacrylate (MMA), and crosslinkers poly(ethylene glycol) dimethacrylate (PEGDMA750) and di(ethylene glycol) dimethacrylate (DEDMA). The ratio of the monomers and crosslinkers are chosen so that the different networks have the same T_g and rubbery modulus, but different swelling ratio ranging from 3–13%. These systems enable us to investigate the effect of swelling ratio on the thermoviscoelastic properties and shape memory behavior. In conjunction with this modeling project, we performed a suite of thermomechanical experiments on the dry polymer and the fully swollen polymer. Our dynamic mechanical analysis (DMA) experiments reveal that swollen material has a more compliant glassy response and a lower T_g . In isothermal uniaxial compression specimens at room temperature and strain rate 0.002/s, the swollen sample is significantly softer than the dry material. The dry material exhibits a viscoplastic response with yielding and post-yield softening, while the swollen material exhibits a viscoelastic response. We also measured the solvent driven unconstrained strain recovery of the material by immersing a specimen, programmed at high temperature in tension, in water.

Significance:

The modeling studies provide a fundamental understanding between thermoviscoelastic properties and thermomechanical loading conditions and the recovery behavior of shape memory polymers, which is needed for the development of computational tools for the efficient design and optimization of SMP materials and devices. Moreover, this research advances the development of a continuum-modeling framework for finite deformation thermoviscoelasticity. By reducing design and manufacturing costs and enabling new and integrated functionalities, the models developed have the potential to significantly impact a broad range of technologies important to DOE and DoD, including medical devices, integrated sensors and actuators, aerospace, and manufacturing.

Effective Programming Tools and Techniques for the New Graph Architecture HPC Machines 149655

Year 3 of 3

Principal Investigator: D. Dechev

Project Purpose:

Large graph problems that arise in complex network analysis, data mining, computational biology, and national security applications have sparked the development of new types of high-performance architectures and codes. These codes involve very large numbers of threads and much greater sharing of information between processors than traditional scientific computing approaches, posing much greater concurrency challenges. Unfortunately, concurrent programming for shared memory multithreaded applications is non-trivial because of the numerous hazards including race conditions, deadlocks, livelocks, and order violations. Such errors are hard to reproduce, often lead to unpredictable real-time behavior and are notoriously difficult to debug. The use of mutual exclusion, the most common synchronization technique for shared data, can lead to significant overhead, high complexity, and reduced parallelism in addition to the mentioned safety risks. Even for conventional multicore systems and datasets of modest size, the use of mutual exclusion can cause convoying effects that, in turn, can seriously affect the application's performance. According to a number of studies at NASA Ames, the current development and validation techniques are prohibitively expensive for problems of such complexity. We are addressing this highly challenging problem by creating a software framework for safe and efficient concurrent synchronization for massively multithreaded shared-memory programs. This approach will be based on the application of lock-free synchronization, a new alternative to mutual exclusion for designing scalable data objects. In our previous work, we have shown that lock-free synchronization eliminates whole classes of concurrency hazards while delivering performance improvements for many scenarios by a large factor. Our goal is to create a portable and generic software platform that will greatly assist domain scientists who are not experts in concurrency theory and formal methods produce highly efficient and correct high performance computing code for solving large graph analysis problems.

Summary of Accomplishments:

Understanding: this research has led to a deeper understanding of the principles for effective design and application of nonblocking data structures for multiprocessor programming. The problem of practical design of nonblocking data structures is known to be difficult.

Discovery: our approach has led to the discovery of new data structure designs, such as a wait-free hash table, a wait-free vector and 14 other related container types, for the development of software applications that fully exploit modern multiprocessor architectures.

Software deliverable: highly reusable open source software library with 16 data structures and other parallel building blocks.

Significance:

Our results allow a new kind of large-scale enabling predictive simulation. The deliverables will provide an immense boost in performance and software reuse, consequently productivity, for developers of scientific and systems applications, which are predominantly in C/C++.

The C++ Standard Template Library is widely used and a concurrent replacement library will have an immediate practical relevance and a significant impact on a variety of parallel programming domains

including enabling predictive simulation, massive data mining, and computational biology. The deliverables will enable software that is substantially more reliable and efficient than the existing state of the art. Data mining applications are relevant to DoD and DHS, while predictive simulation is important to both these and other federal agencies, including DOE/NNSA.

Refereed Communications:

R.A. Ashraf, F. Luna, D. Dechev, and R.F. DeMara, "Designing Digital Circuits for FPGAs using Parallel Genetic Algorithms," in *Proceedings of the 2012 Symposium on Theory of Modeling and Simulation*, 2012.

A. Hall, M. Gabilondo, and D. Dechev, "Using Parallelization to Improve the Efficiency of an Automated Taxi Route Generation Algorithm," *Central European Journal of Computer Science*, vol. 2, pp. 118-127, June 2012.

S. Braeger, N. Arnold, and D. Dechev, "Scalable N-Body Event Prediction," *Central European Journal of Computer Science*, vol. 2, pp. 1-15, March 2012.

D. Bottisti, L. Mendez, and D. Dechev, "CuNeuQuant: A CUDA Implementation of the NeuQuant Image Quantization Algorithm," in *Proceedings of the 16th International Conference on Image Processing, Computer Vision, and Pattern Recognition*, 2012.

A. Vidal, D. Dechev, and A. Kassab, "Evaluation of Two Acceleration Techniques in a Multithreaded 2D Poisson Equation Solver," in *Proceedings of the International Conference on Computational Science*, 2012.

S. Jin, D. Dechev, and Z. Qu, "Parallel Particle Swarm Optimization (PPSO) on the Coverage Problem in Pursuit-Evasion Games," in *Proceedings of the 20th ACM/SIGSIM High Performance Computing Symposium*, 2012.

A. Vidal, A. Kassab, D. Mota, and D. Dechev, "A Multithreaded Solver for the 2D Poisson Equation," in *Proceedings of the 20th ACM/SIGSIM High Performance Computing Symposium*, 2012.

Stochastic Study of Microparticle Adhesion due to Capillary Condensation 150123

Year 3 of 3

Principal Investigator: J. A. Hubbard

Project Purpose:

Advanced diagnostics and experimental methods have been developed to characterize microparticle resuspension and the effects of particle size, capillary condensation, electrostatics, and van der Waals adhesion. Laser Doppler Vibrometry, digital microscopy, and high-speed imaging were used to make in-situ measurements of surface accelerations and corresponding particle resuspension rates.

Microparticle adhesion and resuspension have been studied, where Laser Doppler Vibrometry, digital microscopy, and high-speed imaging were used to characterize the rate of microparticle resuspension due to mechanical impulse forces. The effects of capillary condensation, particle size, electrostatic adhesion, and van der Waals forces have been quantified. The effects of inter-particle cohesive bonds on aggregate-surface adhesion were also observed and quantified. These observations suggest clusters of biological spores may resist resuspension forces due to internal energy dissipation.

Summary of Accomplishments:

Experimental data were used to formulate semi-empirical correlations for percent resuspension as a function of the dimensionless resuspension force. These correlations can be used in existing computational modeling tools, such as the Hazard Prediction and Assessment Capability (HPAC), to simulate the dispersion and fate of radiological, biological, and chemical weapons agents in the atmosphere. Experimental methods developed here can be directly applied to trace detection and remediation of chemical, biological, radiological, nuclear, and explosive materials (CBRNE) and are recommended for studying spore resuspension. Semi-empirical relationships presented in this work can also be integrated into existing hazard prediction and assessment capability tools to incorporate the effects of resuspension in computational. This work constitutes a validation data set for discrete element models (DEM) developed at Sandia, which could be used to model microparticle adhesion and resuspension. These methods can be used for future studies of adhesion and resuspension of CBRNE under realistic atmospheric conditions.

This work constitutes a validation data set for DEM, thereby enabling predictive simulation. DEM models can be used, and should be developed, to study aerosol transport and fate, aggregate adhesion, and the physics of aerodynamic resuspension.

Semi-quantitative observations of particle aggregation illustrate the influence of inter-particle cohesive forces on aggregate-surface adhesion. These observations are particularly relevant to 1) the detection of biological agents, and 2) remediation of critical infrastructure contaminated with biological agents, since they most likely exist as clusters of spores rather than isolated spores. Although semi-qualitative, this observation is the first of its kind and further supports the use of DEM models to study microparticle and aggregate adhesion and resuspension.

Significance:

Experimental methods developed here can be directly applied to trace detection and remediation of chemical, biological, radiological, nuclear, and explosive materials (CBRNE) and are recommended for studying spore resuspension. Semi-empirical relationships presented in this work can also be integrated into existing hazard prediction and assessment capability tools to incorporate the effects of resuspension in computational models. Lastly, this work constitutes a validation data set for discrete element models (DEM) developed at Sandia, which could be used to model microparticle adhesion and resuspension.

Of relevance to DoD and DHS, resuspension of biological particles from terrorist attacks is a significant threat not adequately incorporated into existing hazard assessment and prediction tools. Additionally, our scientific understanding of aerosol resuspension can be improved through experiment and computational modeling. In this study, aerosol resuspension experiments were performed. Experimental methodologies developed in this work represent new and innovative techniques to evaluate spore resuspension for homeland security applications and force protection. Experimental results from this work can also be integrated into existing hazard prediction tools and be used to validate advanced computational physics models.

Refereed Communications:

J.A. Hubbard, J.E. Brockmann, D. Rivera, and D.G. Moore, "Experimental Study of Impulse Resuspension with Laser Doppler Vibrometry," *Aerosol Science and Technology*, vol. 46, pp. 1303-1312, July 2012.

Studies in High Rate Solidification 150638

Year 3 of 3

Principal Investigator: J. D. Madison

Project Purpose:

Sandia is responsible for the quality and well-being of welding and brazes throughout the DOE and NNSA complex with applications ranging from nuclear weapons and nuclear energy to waste storage and renewable energy technologies. High rate solidification joinings are multi-tiered, multi-physics processes. Prior investigations at Sandia have focused primarily on macroscale studies beyond the level of the microstructure and have been largely phenomenological and process or component-driven in scope. While still challenging, 3D reconstructions of experimentally derived microstructures of appreciable scale and resolution are becoming increasingly possible due to recent advances in experimental tools, computational power and data storage and have allowed incremental increases in the understanding of material systems, material microstructure, and material properties.

Investigation of the linkage between processing and resultant microstructure have been pursued through investigation of high rate solidification events found in laser welds of 304L stainless steel. A variety of standing-edge joints utilizing a continuous wave Nd:YAG laser have been produced and examined in a 304-L stainless steel to advance fundamental understanding of the linkage between processing and microstructure in high-rate solidification events. Acquisition of 3D reconstructions via micro-computed tomography combined with traditional metallography has allowed for qualitative and quantitative characterization of weld joints in a material system of wide use and broad applicability. The presence, variability, and distribution of porosity has been examined for average values, spatial distributions and morphology and then related back to fundamental processing parameters such as weld speed, weld power, and laser focal length.

Summary of Accomplishments:

In this work, a methodical evaluation of laser-weld parameter space encompassing five discrete welding speeds over six different delivered powers and two separate focal lenses were employed for quantifying microstructure variation and the effect on material properties in laser weldments. Process parameter maps relating laser focal length, delivered power, and welding speed to averages, maximums, minimums, and full distributions of porosity size, shape, orientation and frequency were determined for the aforementioned laser welds in 304L stainless steel.

Significance:

In this project, a thorough set of 3D metrics for quantifying the presence of microstructure features was developed and a framework to pass such quantitative metrics on to continuum-level mechanical response models was created. This work has direct applicability to life extension efforts and also facilitates an improvement in Sandia's ability to support welds and joinings throughout the entire DOE/NNSA complex.

Refereed Communications:

J. Madison and L.K. Aagesen, "Quantitative Characterization of Porosity in Laser Welds of Stainless Steel," *Scripta Materialia*, vol. 67, pp. 783-786, November 2012.

Quantifiably Secure Power Grid Operation, Management, and Evolution 151288

Year 2 of 3

Principal Investigator: J. Watson

Project Purpose:

This project will develop decision-support technologies to enable rational and quantifiable risk management for the key grid operational timescales.

Risk or resiliency metrics are foundational in this effort. The 2003 Northeast Blackout investigative report stressed the criticality of enforceable metrics for system resiliency — the grid's ability to satisfy demands subject to perturbation. However, we lack well-defined risk metrics for addressing the pervasive uncertainties associated with renewables generation, and decision-support tools for their enforcement, thus severely impacting efforts to rationally improve grid security.

For second-to-minute timescales, robust control systems must mitigate the impact of failure cascades, forming self-sustaining island network topologies to facilitate rapid service restoration. For day-ahead unit commitment, decision-support tools must account for topological security constraints, economic costs, and supply and demand variability — especially given high renewables penetration. For long-term planning, transmission, and generation expansion must ensure that realized demand is satisfied for projected technological, climate, and growth scenarios. The timescales are tightly coupled and, consequently, must be studied in concert.

Our decision-support tools will analyze and enforce tail-oriented risk metrics for explicitly addressing high-consequence events. Historically, decision-support tools for the grid consider expected cost minimization, largely ignoring risk and, instead, penalizing loss-of-load through artificial parameters.

Our technical focus is the development of scalable solvers for enforcing risk metrics. We will develop advanced stochastic programming solvers to address generation and transmission expansion and unit commitment, minimizing cost subject to pre-specified risk thresholds. Despite significant promise, major algorithmic challenges remain to address regional and national grid scales. With renewables, security critically depends on production and demand prediction accuracy. We will use powerful filtering techniques for spatiotemporal measurement assimilation to develop short-term predictive stochastic models. Novel robust control algorithms will be developed to enforce risk thresholds for unit commitment and failure cascade mitigation. These algorithms currently and unrealistically (given renewables) assume tightly bounded uncertainties.

Predicting Structure-Property Relationships for Interfacial Thermal Transport 151289

Year 2 of 3

Principal Investigator: E. S. Piekos

Project Purpose:

Microsystems are a key component in a vast array of applications, impacting most Sandia mission thrusts. Over time, microsystems designers have increased the number of material regions in a typical device while decreasing their spatial extent. From a thermal perspective, this trend increases the relative importance of interfacial transport compared to traditional bulk transport. Increasingly, interfacial thermal transport is an important factor in numerous Sandia-developed microsystems including high-power electronics, coolers for space-based sensors, microelectromechanical systems (MEMS), and thermoelectric power modules. Predictive tools are therefore essential for characterizing existing designs under uncertainty in manufacture and operation, as well as for leveraging interfacial transport to enhance functionality in future designs.

Current models for interfacial thermal transport are inherently limited due to the nearly ubiquitous assumption of a perfect boundary. As a result, the transport is treated as an intrinsic material property, independent of interface structure, despite ample experimental evidence to the contrary.

We propose to develop a predictive tool for thermal transport through realistic interfaces. This tool will provide experimentally validated structure-property relationships for nanostructural features, including interfacial dislocations and compositional intermixing. It will be developed through a “bottom-up” computational approach, combined with systematic fabrication, disruption, and characterization of interfaces.

Interfacial thermal transport at imperfect boundaries is an inherently multiscale problem with many interacting effects arising from the fact that lattice perturbations can extend over many unit cells and many types of defects can exist simultaneously. An organized inquiry, therefore, places great demands on simulation, sample fabrication, microstructural characterization, and thermal transport measurement — all of which must be performed in close communication with one another to disentangle competing effects. Sandia’s strength in all these areas provides a unique opportunity to perform such an inquiry and replace decades-old simplifications with validated physics-based models.

Physics-Based Multiscale Stochastic Methods for Computational Mechanics of Heterogeneous Materials

151291

Year 2 of 3

Principal Investigator: J. B. Lechman

Project Purpose:

Classical continuum models of transport in complex, heterogeneous systems (groundwater contaminant transport, charge carrier transport/storage in composite electrodes) frequently struggle to give reliable results while detailed microscopic methods (molecular dynamics) are computationally prohibitive at large scales. However, it is often unrecognized that these systems exhibit related phenomena that can serve as a unifying basis for a generalization of continuum mechanics beyond classical assumptions. Common features include long-range correlations and multiple overlapping/competing length and time scales, which render suspect the classical assumptions of scale separation and “slowly” varying mass, momentum, and energy densities. Recent developments in nonlocal models make it possible to relax classical continuity assumptions without sacrificing mathematical verification, computational feasibility or model validation. Hence, we seek nonlocal models, which are thermodynamically and physically consistent at scales intermediate to the atomistic (micro) and component/process (macro) scales. As an archetypal heterogeneous material, we will develop a physically based, mesoscale, stochastic continuum model of colloidal suspensions (diffusive transport in random media).

Although some recent effort has focused on spatial and temporal nonlocality in various systems, we will develop models in the framework of nonlocal calculus by connecting nonlocal master equation models to underlying physical stochastic processes. This avoids assumptions that create difficulties for capturing inherently nonlocal phenomena (e.g., “cooperative”/correlated dynamics, or non-Fickian behavior). This is a novel approach that distinguishes Sandia’s capabilities. Many seek to capture these features through higher-order gradient expansions of relevant fields or through homogenization. We seek to capture nonlocal effects through integral equation formulations as opposed to partial differential equation-based models. A high-risk focus of this effort will be establishing the physical basis of the approach in terms of correlation lengths and times and the link between microscopic correlated dynamics and mesoscale statistics for the model system.

Network and Ensemble Enabled Entity Extraction in Informal Text (NEEEEIT) 151292

Year 2 of 3

Principal Investigator: W. P. Kegelmeyer

Project Purpose:

Much of the world's actionable information is locked up in increasingly unmanageable volumes of text. This has inspired work in "entity extraction" (EE), which is the detection of meaningful terms in text: persons, places, dates, etc. Robust, accurate entity extraction is the crucial first step for all information extraction from text; you can't "connect the dots" unless you identify the dots in the first place.

Entity extraction research has so far focused on clean, edited, "formal" text. Unfortunately, much of the information of interest is in personal, "informal" text, such as email or blogs. These differ from the Medline abstracts and Reuters news stories commonly studied in that they tend to be riddled with errors of spelling and grammar, abbreviations, and a terseness and obliquity of reference borne of the context shared by sender and receiver. The informal text domain has received scant study — just enough to show that it causes the performance of existing methods to drop precipitously.

We propose to vastly improve the accuracy of entity extraction in informal text, via application of Sandia-specific expertise in "ensemble" machine learning methods. Further, we will exploit new high-performance computing network capabilities to permit the integrated analysis of a full conversational thread. The potential of this approach is recognized, but scaling issues have, prior to recent Sandia work, prevented their exploration.

By creating methods to make accurate entity extraction in informal text possible, and by leveraging Sandia's investments in informatics frameworks, we will deliver a system that starts with raw email or blogs and produces high quality entity identification, suitable for search, linking, visualization, and analysis.

Kalman-Filtered Compressive Sensing for High-Resolution Estimation of Anthropogenic Greenhouse Gas Emissions from Sparse Measurements at Global Scale

151293

Year 2 of 3

Principal Investigator: J. Ray

Project Purpose:

The project seeks to develop techniques to infer the spatiotemporal distribution and dynamics of CO₂ emissions and uptake (i.e., anthropogenic and biospheric fluxes, from sparse observations of CO₂ concentrations). Such a characterization is critical to understanding the carbon cycle and, therefore, predicting future climate variability and its important role in the verification of international CO₂ abatement treaties and management of mitigation programs. Accurate emissions characterization requires numerical simulations of atmospheric transport, conditioned on sparse data, with simultaneous quantification of uncertainties. An inverse problem can be formulated to reconstruct the location/character of CO₂ emissions and sequestration by minimizing the difference between observations and predicted values, subject to other known constraints. Many technical challenges arise however: 1) large, ill-conditioned linear systems result from sparse measurements and complex diffusive dynamics, 2) extreme computational resources are required to address the high dimensionality of the uncertainty space, and 3) a consistent and complete statistical framework is necessary for characterization of uncertainty. This project addresses these issues through adaptation of novel image reconstruction techniques, efficient data assimilation methods, multiscale algorithms, and geostatistical Bayesian inverse methods.

We will develop Bayesian techniques to reconstruct time-variant, spatial fields from limited measurements, by integrating concepts from compressive sensing (CS), Ensemble Kalman Filters (EnKF), and multiscale modeling. CS exploits sparse basis sets to achieve accurate multiscale field/image reconstruction from limited data. We will extend these approaches to dynamic fields such as CO₂ emissions and uptake, and integrate these techniques with efficient data assimilation methods. To this end, EnKF provides the necessary balance of computational efficiency and robust uncertainty characterization, as well as an avenue to explore assimilation of multiscale observations. Our algorithmic development will focus on supporting the CO₂ source flux estimation problem as a fundamental technical capability but will be sufficiently general to be directly relevant to many problems in science and engineering.

Multiscale Modeling for Fluid Transport in Nanosystems 151294

Year 2 of 3

Principal Investigator: J. A. Templeton

Project Purpose:

Fluid transport processes at the nanoscale play an important part in the performance of many nanosystems, such as Li-ion batteries, supercapacitors, and gas-phase detectors. A commonality in these devices is that they often consist of nanoscale components (interfaces, pores, etc.) connected to a much larger bulk reservoir system. Interaction with the bulk critically affects the performance of the nanosystem since the same fluid exhibits different behavior at different scales via high concentration gradients and chemical reactions. Two-way feedback between these scales is required to accurately predict system response. For example, the high-voltage double layers that form in electrical energy storage devices deplete the electrolytic ion concentration, thereby modifying the transport to the double layer. Capturing this feedback is complicated because different simulation approaches are required for the nanoscale features and the bulk flow. Atomistic simulation can model the complexity of nanodevices, but is intractable for the bulk. Therefore, the bulk must be resolved using macroscale simulation approaches (e.g., finite elements). New algorithms are needed to accurately account for time dependent mass, momentum, and thermal transport between these two regions while capturing all the physics needed for accurate device simulation, including electric fields and chemistry.

Statistically Significant Relational Data Mining 151295

Year 2 of 3

Principal Investigator: C. A. Phillips

Project Purpose:

In many data mining applications, especially the search for “unexpected” or “significant” structure in graph-based social information, it is difficult to specify exactly what one is seeking. For example, given a graph where nodes represent people and edges represent relationships between people, there is general agreement that a community is a set of nodes more connected internally than to the rest of the graph. But no formal graph theoretic definition of connectedness seems to capture what a human perceives to be the correct communities in all cases. Most community detection algorithms combine approximate optimization of a metric with ad hoc statistical methods. To date, there are no rigorous ways to determine whether an algorithm has succeeded in finding the “correct” answer in a real data set, or even in specially constructed benchmarks. Similar questions arise in other graph-data-mining problems that search for specific patterns, or attempt to explain (dynamic) relationships.

We will develop statistically rigorous methods for understanding and testing the significance of graph properties and structures. These methods can be incorporated into data mining algorithms either integrally, or as a postprocessing “acceptance” test. We will develop methods to create benchmarks for specific data mining problems that hide a known solution without destroying it. These benchmarks would provide confidence in algorithms’ absolute and relative performance.

Bayesian methods offer one plausible approach. Each graph problem provides unique challenges. We must formally describe a priori domain knowledge and constraints (“prior distributions”). We must create plausible random graph models, describing the ways a community, pattern, etc., might evolve from these distributions. Subsequently, we must compute conditional probabilities that characterize the most likely solutions given the structure of the input instance. Although the general methods are well known to statisticians, they require customization to the structure of each problem. These methods have not been applied to evaluating the correctness of efficient graph algorithms.

Integrated Nano- and Quantum Electronic Device Simulation Toolkit 151297

Year 2 of 3

Principal Investigator: R. P. Muller

Project Purpose:

The next generation of semiconductor devices will have to confront quantum mechanical effects, including phenomena to be avoided, like gate leakage, as well as new behavior that can be harnessed, like entanglement. Few-electron nanodevices have been developed to use entanglement in quantum computing and sensing beyond the traditional quantum limits, but the resulting entangled device states are extremely sensitive to atomic-scale effects that are not traditionally considered in nanoelectronics modeling. The community is presently without a multiscale simulation capability that appropriately captures how atomic-scale phenomena propagate through to the mesoscale device physics.

To describe these devices, we need to enhance existing device simulators in several ways. Quantum mechanical effects must be accounted for by solving the coupled system of the Schrodinger and Poisson equations. Where atomic-scale effects, such as the multiple valleys in silicon, are important, tight binding solutions for electronic wave functions are necessary for predictive simulations. Furthermore, in systems with many-electron excited states, configuration interaction techniques are needed to properly capture multielectron wave functions.

We are developing a suite of tools that includes Schrodinger-Poisson, tight binding, and configuration interaction capabilities, and thereby addressing current and future issues critical to simulating quantum-scale electronic devices.

Control and Optimization of Open Quantum Systems for Information Processing and Computer Security

151299

Year 2 of 3

Principal Investigator: M. Grace

Project Purpose:

The purpose of this project is to: 1) explore the fundamental limits of controlling quantum systems and 2) analyze the implications of these limits, especially in the context of quantum information processing (QIP). Achieving the error threshold for fault-tolerant QIP is extremely difficult given device/control fluctuations, experimental constraints, and the unavoidable coupling of a quantum computer to its surrounding environment. Based on recent results by this team and academic/industrial collaborators, we are developing a crucial enabling technology, namely, the ability to control and explore processes at the atomic level, computationally, especially in the presence of uncertainty and time-dependent noise. This work will provide a tool to guide experimentalists and theoreticians in creating practical QIP controls and devices. During FY 2012, we developed two numerical methods to simulate time-dependent stochastic quantum systems (SQS) efficiently, compared to simulations based on Monte Carlo methods. These methods will be used in optimal control (OC) calculations, which require multiple sequential simulations to achieve convergence. Monte Carlo methods for these calculations are expensive and scale unfavorably with the dimension of SQS, hence the need for an alternative. Combining our numerical methods and OC simulations will allow us to quantify the limits of control for realistic SQS. Another goal of our project is to mathematically analyze the critical structure of the quantum-control landscape for SQS (i.e., identifying the fraction of critical points corresponding to global extrema, local extrema, and saddles). While numerical simulations produce OC solutions for SQS, a mathematical analysis of the landscape would reveal the general underlying structure of this control problem. Knowledge of this structure can influence profoundly the choice of algorithms used to locate OCs and the design of quantum technologies.

On Strongly Coupled Partitioned Schemes for Solving Fluid-Structure Interaction Problems using High-Order Finite Element Models Based on Minimization Principles

151383

Year 2 of 2

Principal Investigator: J. D. Thomas

Project Purpose:

High-order formulations for solving fluid-structure interaction problems using the finite element method will be developed and implemented. The C0 Lagrange type, higher-order, spectral finite elements will be employed for all numerical discretizations. The solid will be modeled using a finite strain St. Venant Kirchhoff constitutive model; likewise, the laminar fluid will be described by the incompressible Navier-Stokes equations. The use of a single high-order numerical framework, namely the finite element method, will allow for enhanced compatibility and accuracy in the physical coupling of the fluid and structure. In the interest of achieving an ideal variational setting for the numerical formulation, all finite element models will be constructed using minimization principles. The solid mechanics problem will be discretized using traditional weak formulations while least-squares finite element models will be employed for the viscous fluid. Least-squares formulations will naturally avoid shortcomings associated with weak formulations of the Navier-Stokes equations, such as the inf-sup condition and the need for numerical upwinding. The viscous flow equations will be expressed with respect to an arbitrary Lagrangian-Eulerian reference frame, thus allowing for the use of a fluid mesh that evolves with time. Motion of the fluid mesh will be achieved through the use of standard pseudo-elasticity procedures. Strong coupling between the fluid and solid will be enforced using implicit strongly coupled partitioned procedures. Various relaxation, prediction and approximate Newton methods will be employed in the context of the partitioned approach. The Schur complement method will be used to condense out all element level interior nodes from the global set of finite element equations. Overall performance of the numerical formulations will be assessed by solving benchmark problems of particular interest to Sandia. The work is in collaboration with Texas A&M University.

Summary of Accomplishments:

We consider the application of high-order spectral/hp finite element technology to the numerical solution of boundary-value problems arising in the fields of fluid and solid mechanics. For many problems in these areas, high-order finite element procedures offer many theoretical and practical computational advantages over the low-order finite element technologies that have come to dominate much of the academic research and commercial software of the last several decades. Most notably, we may avoid various forms of locking which, without suitable stabilization, often plague low-order least-squares finite element models of incompressible viscous fluids as well as weak-form Galerkin finite element models of elastic and inelastic structures.

The research documented in this project includes applications of spectral/hp finite element technology to an analysis of the roles played by the linearization and minimization operators in least-squares finite element models of nonlinear boundary-value problems, a novel least-squares finite element model of the incompressible Navier-Stokes equations with improved local mass conservation, weak-form Galerkin finite element models of viscoelastic beams and a high-order, seven parameter continuum shell element for the numerical simulation of the fully geometrically nonlinear mechanical response of isotropic, laminated composite and functionally graded elastic shell structures. In addition, we also present a simple and efficient sparse global finite element coefficient matrix assembly operator that may be readily parallelized for use on shared memory systems. We demonstrate, through the numerical

simulation of carefully chosen benchmark problems, that the finite element formulations are efficient, reliable and insensitive to all forms of numerical locking and element geometric distortions.

Significance:

In this project, we have presented finite element formulations for fluid and solid mechanics problems using high-order spectral/hp finite element technology. Our primary objective has been to adopt novel mathematical models and innovative discretization procedures wherein the additional benefits of employing high-order spectral/hp finite element technology are pronounced. We find that for many such problem sets, high-order finite element procedures offer the prospect of highly accurate numerical solutions that are completely devoid of all forms of locking. As a result ad-hoc tricks (e.g., reduced integration and/or mixed interpolation) required to stabilize low-order finite element formulations are unnecessary. Solutions of such problems have application in various areas of interest to DOE/NNSA and DHS.

Refereed Communications:

V.P. Vallala, G.S. Payette, and J.N. Reddy, “A Spectral/hp Nonlinear Finite Element Analysis of Higher-Order Beam Theory with Viscoelasticity,” *International Journal of Applied Mechanics*, vol. 4, March 2012.

G. S. Payette, K.B. Nakshatrala, and J.N. Reddy, “On the Performance of High-Order Finite Elements with Respect to Maximum Principles and the Nonnegative Constraint for Diffusion-Type Equations,” *International Journal for Numerical Methods in Engineering*, vol. 91, pp. 742-771, May 2012.

Modeling Reactive Transport in Deformable Porous Media using the Theory of Interacting Continua

152507

Year 2 of 2

Principal Investigator: D. Z. Turner

Project Purpose:

Recent reports illustrate growing international interest in using carbon-dioxide (CO₂) sequestration in geological formations to reduce greenhouse emissions. If implemented on the scale needed to make noticeable reductions in atmospheric CO₂, a billion metric tons or more must be sequestered annually (a 250-fold increase over today's amount). Unfortunately, existing simulation codes lack robust capabilities for modeling these problems. In addition, a number of other problems of critical interest to the DOE and Sandia, including long-time storage of nuclear waste, seepage of contaminants, and pyrotechnics, allude to the paramount need for robust numerical methods for reactive transport in deformable porous media.

The research is guided by the following hypothesis: a treatment of reactive transport in deformable porous media using the Theory of Interacting Continua and from a differential algebraic equation (DAE) perspective, with an emphasis on stability, accuracy and efficiency, will enable tremendous capabilities for solving complex fluid-solid-chemical interaction problems of particular national interest. As opposed to existing methods, which treat the underlying equations exclusively as ordinary differential equations (ODEs), we are employing numerical techniques from the DAE literature that respect the stability and order-of-accuracy of DAE solvers, which are not addressed by standard ODE-based solvers. Furthermore, existing approaches for fluid-solid interaction (FSI) assume that the fluid and solid occupy separate distinct domains interacting only at a global-scale interface. This class of methods is not applicable for transport in deformable porous media because in these problems the fluid and solid essentially occupy the same domain (the flow occurs inside the void space of the solid). To address the coincident nature of these problems, we will use the Theory of Interacting Continua, which homogenizes both constituents, allowing them to co-occupy the domain occupied by the mixture. This approach will lead to broad application in a wide variety of important problems.

Summary of Accomplishments:

In this project, we have developed a computational methodology for analyzing engineering problems involving flow-induced damage of porous materials using a mixture theory-like approach. The numerical formulation involved coupling two simultaneous simulations that track chemical reactions, flow characteristics, and damage evolution. The formulation was demonstrated for a wide variety of problems including carbon dioxide sequestration, hydraulic fracturing, and energetic materials. We showed the types of problems this methodology is appropriate for and demonstrated its features. We developed a technology able to address many of the needs not currently met by existing methodologies.

Significance:

The ultimate goal of this research is to address a number of engineering problems of national interest that depend critically on the ability to model flow-induced damage of porous materials. The research reported herein has DOE-relevant applications in geologic sequestration of anthropogenic carbon dioxide, ignition processes for energetic materials, and prediction of crack pervasiveness and hydrocarbon yields for hydraulic fracturing.

Automated Exploration of the Mechanism of Elementary Reactions 153342

Year 2 of 2

Principal Investigator: J. Zador

Project Purpose:

Optimization of new transportation fuels and engine technologies requires characterization of the combustion chemistry of a wide range of fuel classes. Theoretical studies of elementary reactions, the building blocks of complex reaction mechanisms, are essential to accurately predict important combustion processes such as autoignition of biofuels. The current bottleneck for these calculations is a user-intensive exploration of the underlying potential energy surface (PES), which relies on the “chemical intuition” of the scientist to propose initial guesses for the relevant chemical configurations. For newly emerging fuels, this approach cripples the rate of progress because of the system size. Developing the necessary computational tools for an automated stationary point search that also interfaces to our already existing chemical kinetic tools will represent a game-changing advance that addresses the critical path on the development of key elementary reaction mechanisms necessary for the optimization of new fuels for the 21st century, in line with the energy mission area of Sandia.

Published methods for automated identification of relevant chemical structures are computationally expensive due to their general nature. Also, these methods do not take advantage of the large body of chemical knowledge (i.e., the approximate structures that are relevant can be predicted or are known for the majority of the reactions). The problem that researchers in theoretical chemical kinetics often face is not the proposal of a new chemical pathway, but rather the actual execution of the related calculation, which currently requires a significant quantity of human interaction.

The algorithm incorporates a fundamentally new approach by integrating chemical knowledge in the code and will significantly accelerate and almost completely automate the exploration of the possible pathways in elementary reactions relevant to combustion. Efficient exploration of these high-dimensional spaces involves significant algorithmic and computational challenges, requiring the combination of state-of-the-art tools of various research areas.

Summary of Accomplishments:

We created software named KinBot that enables the automated search in elementary reaction kinetics. Currently already a handful of very general reaction types are implemented, and we have shown that our approach is efficient and feasible. For the current 1.0 version of the code, we focused on the chemistry that occurs during low-temperature autoignition processes, which represents a wide variety of chemical transformations, playing a role also in atmospheric chemistry. The code will be continuously extended by new formal reaction types, but already covers a wide variety of chemistry. KinBot is a parallel C code, which combines a growing network approach with a chemistry-based method. It has been successfully applied to several chemical systems under current investigation.

Significance:

Dependence of fossil and other fuels is a topic of national interest and one germane to the energy missions of Sandia and DOE. One way to reduce this dependence is to burn fossil fuels more efficiently and/or add alternative fuels to the stream. Currently, our ability to achieve these goals is hindered by the vast variety of chemical compositions, especially in fuels derived from biological sources. Modern (clean and efficient) engine technologies operating under lean conditions show a much larger sensitivity to chemical kinetics, and require a detailed characterization of the chemistry at the molecular level. Our effort contributes to this overall goal by significantly accelerating current computations.

MultiPhysics Modeling of Environmentally Activated Network Polymers 153890

Year 2 of 2

Principal Investigator: K. N. Long

Project Purpose:

Environmentally activated polymers (EAP) exhibit complex mechanical behavior in response to external stimuli such as exposure to light at specified wavelengths or to temperature change within the material. These environmental-mechanical couplings make possible “smart” EAP applications including: 1) thermally removable encapsulation for electronics packaging, 2) photo-activated flaw mitigation in polymer structures, and 3) thermally or photomechanically generated surface patterns for microfluidics and sensors.

However, the state of the art for many EAP systems is limited to simple characterization and demonstration experiments, which are inadequate to describe their environmental-mechanical behaviors in sophisticated, application-oriented settings. Therefore, the critical scientific need to enable use of EAPs is the development of theoretical and computational tools necessary to guide EAP design efforts.

This project endeavors to address that need by formulating mechanistically driven, continuum-scale, multiphysics material models that will be implemented into the SIERRA Mechanics finite element architecture for two EAPs activated by thermal and photo stimuli respectively. There are several challenges to achieve these endeavors. Modeling photo and thermal chemistry and their couplings to the microstructural evolution of polymer networks is difficult. It is also challenging to determine how such changes are coupled with the continuum mechanical response. Investigating these issues will be useful in future material modeling efforts at Sandia along with the material models, which can be used as needed in future projects.

Summary of Accomplishments:

The project naturally divided into modeling photochemically and thermal-chemically responsive polymers.

Our goal, with respect to photochemically responsive polymers, was to explore and control the folding of polymer sheets with light. We labeled this process photo-origami. We were motivated both to demonstrate new capabilities as well as to examine a system potentially useful in novel sensing and actuation scenarios. We used simulations to design multiple step mechanical deformation and photo-masked irradiation protocols to generate complex 3D shapes such as a heart and a box and then realized such shapes experimentally. We also examined using photomechanical protocols to develop and control elastic instabilities in responsive polymer films. Our models successfully predicted experimental results from many different photomechanical scenarios.

Our goal, with respect to the thermal-chemically responsive network polymers, was to develop a thermal-chemical-mechanical constitutive model, validate it against data in the literature, and examine the difference in behavior between these materials and conventional network polymers. We successfully generated a constitutive model, implemented it into Sierra/SM, and successfully predicted the time and temperature dependent response of this polymer with data in the literature. We examined scenarios in which these materials differed in behavior compared with conventional network polymers. Two key results came out of these efforts:

1) under thermal-mechanical cycling, thermal-chemically-responsive polymers will show substantially different behavior from conventional network polymers if the glass transition is below the temperature

range of the thermal cycle. Under such conditions, the permanent shape of the thermal-chemically responsive polymer will change rapidly and relieve the state of stress. This result has important ramifications in encapsulation and 2) thermal-chemically responsive polymers can be annealed so that the residual stress state can be controlled.

Significance:

The development and validation of photo-chemical-mechanically responsive network polymers to enable photo-origami marks advancements in multiphysics constitutive modeling, as well as in the design and use of light-activated polymers.

The development of a constitutive model for thermal-chemically responsive network polymers enables the prediction of the physical aging behavior of materials, that are of great interest to NNSA. This model constitutes a new predictive capability. The results from this project outlined the circumstances in which these materials differ substantially from conventional network polymers and, therefore, indicate when this new capability should be used.

Refereed Communications:

J. Ryu, M. D’Amato, X. Cui, K.N. Long, H. J. Qi, and M.L. Dunn, “Photo-Origami-Bending and Folding Polymers with Light”, *Applied Physics Letters*, vol. 100, p. 161908, 2012.

Combinatorial Optimization with Demands 154002

Year 2 of 2

Principal Investigator: O. D. Parekh

Project Purpose:

In many practical discrete optimization and resource allocation scenarios, commodities such as bandwidth are discounted when purchased in bulk and piping and cabling may only be available in a small number of types of varying capacity and cost. Such scenarios result in a nonlinear relationship between cost and capacity, which may be modeled infusing traditional combinatorial optimization models with a feature called demands. Thus, the challenge is to design algorithms for models endowed with demands while leveraging the rich and immense mathematical infrastructure developed for traditional linear and discrete optimization. Even without considering economies of scale or demands, most of the underlying problems we consider are already NP-hard (nondeterministic polynomial time) — a means of mitigating this is designing an approximation algorithm, an efficient heuristic algorithm that provably produces a high-quality solution.

We are developing approximation algorithms for resource allocation problems that exhibit economies of scale and are modeled using demands. We aim to accomplish this by generalizing a celebrated technique called iterative rounding that has been instrumental in resolving several open problems since its inception late last decade. While iterative rounding is difficult to adapt to the types of resource allocation problems we consider, even without economies of scale, our method is designed to handle these hurdles while retaining many of the elegant properties of iterated rounding. In addition, we seek to unearth deeper connections between well-understood discrete optimization problems and their significantly more complex demand-endowed counterparts. We expect that such insights will generally help us better understand and model the latter, which are frequently encountered in different application-oriented contexts. A particularly powerful feature of our method is that it implicitly produces a diverse collection of near-optimal solutions, which is useful for uncertain or multiple objective functions.

Summary of Accomplishments:

Our most significant contribution is devising a new framework called iterative packing that offers a unified approach for designing approximation algorithms for packing type resource allocation problems. A decade-old breakthrough called iterative rounding has been instrumental in elegantly resolving several open problems. Iterative rounding is remarkable in that it is a conceptually simple idea that has been able to succeed where much more intricate approaches have failed; however, iterative rounding only applies to a class of problems called covering problems. Our iterative packing framework is the first unified approach to offer many of the advantages of iterative rounding in the context of packing and resource allocation problems. In particular, iterative packing results in simple algorithms with excellent worst-case performance guarantees.

We were extremely successful in leveraging iterative packing to construct new approximation algorithms with significantly improved performance guarantees for several packing problems. Moreover, we proved mathematically that the performance guarantees offered by our algorithms match a well-known and natural bound, hence our algorithms are likely close to best possible. By exhibiting such algorithms, we have resolved an open problem in the field.

Significance:

Resource allocation problems are abundant in applications of national interest, and more accurately modeling economies of scale could have an impact on national security missions and applications for diverse federal agencies. Our new iterative packing framework offers the potential of simple and improved algorithms for such resource allocation problems. Furthermore, the framework may readily be integrated into integer programming solvers such as Sandia's Parallel Integer and Combinatorial Optimizer (PICO) solver.

Refereed Communications:

R.D. Carr and O. Parekh, "Approximating a Capacitated 2-Edge-Connected Spanning Subgraph Problem," to be published in *Operations Research Letters*.

Improved Performance and Robustness of Scalable Quantum Computing 154059

Year 2 of 2

Principal Investigator: C. Brif

Project Purpose:

Quantum information science and technology (QIST) hold the promise of revolutionizing computer science and physics. Of particular importance is the potential capability of a quantum computer (QC) to efficiently solve problems that are believed to be intractable on a classical computer. However, significant outstanding challenges exist, such as implementation of scalable quantum computing systems. While few-qubit operations have been demonstrated, realization of a scalable multi-qubit QC has proven elusive. At the heart of this challenge is the problem of robustness of QCs to control noise. External controls are necessary to enact quantum logic operations and inevitable control fluctuations result in gate errors in realistic QCs. Characterizing the control noise effect on the QC performance and developing robust control strategies for scalable multi-qubit architectures is crucial for advancement of practical quantum computing.

Building on our expertise in control and optimization of quantum information systems, we are developing powerful analytical methods and numerical optimization tools necessary for exploring and enhancing the robustness of realistic multi-qubit QCs to control noise. A critical open question is how the noise-induced errors scale with the QC size in the presence of unwanted inter-qubit couplings. The robustness analysis will utilize properties of the quantum control landscape that relates the physical objective (the quantum computation fidelity) to the applied controls. Optimal controls with enhanced robustness will be identified by using two complementary approaches: 1) landscape characterization in the vicinity of the optimal control manifold and 2) multi-objective optimization that explicitly incorporates the requirement of high robustness. The proposed research will aim at developing a crucial enabling technology, namely, the ability to assess and improve the performance of scalable quantum computing in the presence of control noise; thereby, advancing Sandia's overall efforts in critical areas of QIST.

Summary of Accomplishments:

In this project, we formulated the problem of robust control of quantum gates in the presence of random noise and expressed the dependence of the expected gate fidelity on noise characteristics. Specifically, we employed a perturbative method to obtain an approximate result for the statistical expectation value of the gate fidelity in the presence of weak, random noise in control fields. We used extensive numerical simulations to demonstrate that this approximate result is in excellent agreement with direct Monte Carlo averaging over noise process realizations for fidelity values relevant for practical quantum computing. The developed formalism provides a very efficient way to evaluate the expected gate error for any given noise model. In particular, for white noise, we evaluated the expected gate fidelity analytically and discovered that maximizing the robustness to additive/multiplicative white noise is equivalent to minimizing the total control time/fluence. Since there exist minimum time and minimum fluence required to reach the target quantum transformation, this discovery establishes a direct relationship between the target reachability and robustness to white noise in quantum computing systems. These results were used to estimate how errors induced by white noise in multi-qubit gates scale with respect to the number of qubits. Finally, the approximate method developed in this project is essential for efficiently optimizing the robustness of quantum gates to weak colored noise. We employed stochastic and gradient-based optimization algorithms to identify control fields that exhibit maximum robustness to practically relevant random noise processes. In particular, we demonstrated that the degree of robustness improvement achieved by the optimization increases with the noise correlation

time. The powerful analytical and numerical tools developed in this project for assessing and optimizing the robustness to control noise are expected to be of great value for improving the performance of scalable quantum computing systems in the laboratory.

Significance:

This project is strongly related to the Cybersecurity Protection program of the DOE National Security efforts, which calls for new technology to “preserve the integrity, reliability, availability, and confidentiality of important information.” Quantum computing has the potential to radically alter the character of cybersecurity problems, which makes the results of the project highly relevant to the long-term aspects of the National Cybersecurity Division of the DHS. The project addresses some of the most critical challenges facing the development of scalable quantum computers and thus is likely to have a significant impact on quantum information science and technology.

Refereed Communications:

K.W. Moore, C. Brif, M.D. Grace, A. Donovan, D.L. Hocker, T.-S. Ho, R.B. Wu, and H. Rabitz, “Exploring the Tradeoff between Fidelity and Time Optimal Control of Quantum Unitary Transformations,” *Physical Review A*, vol. 86, p. 062309, December 2012.

A Geometrically Explicit Approach to Adaptive Remeshing for Robust Fracture Evolution Modeling

154317

Year 2 of 2

Principal Investigator: M. Veilleux

Project Purpose:

The purpose of this project is to develop a high-fidelity, geometrically accurate approach to modeling fracture. However, analysts cannot adequately predict failure propagation, or uncertainty thereof, using common modeling approaches. Such approaches typically reduce model complexity at the cost of physical fidelity by smearing crack behavior or limiting crack locations to mesh dependent paths.

Here, we seek to model the cause and uncertainty of failure by explicitly representing fracture (i.e., arbitrarily nonplanar evolution of geometrical facets [fracture surfaces] driven by nonuniform load distribution and resisted by heterogeneous material toughness). The primary focus is on accurate geometrical representation of fracture through local topology and mesh adaptation. However, to facilitate accurate physical representation, we propose to address other challenging research topics in fracture (e.g., material bifurcation; nonlocal regularization; and mapping history-dependent variables).

Although geometrically explicit fracture representation has been commonplace for over twenty years, computational and algorithmic demands have stalled extension of such approaches to complex crack evolution processes. Adaptive crack insertion and propagation routines are not available in current production codes, and such routines in research codes are generally limited to linear elastic fracture mechanics and well-behaved elastic-plastic fracture mechanics applications that rely on criteria and do not model failure process evolution.

We are combining knowledge in adaptive crack modeling and meshing with the high-performance computational capabilities at Sandia to bring to fruition the extensive rewards of geometrically explicit modeling of arbitrarily nonuniform fracture evolution. The approach is applicable for multiple length scales and fracture mechanisms, but, for proof of concept, this study focuses on representing macroscale ductile fracture.

Summary of Accomplishments:

We achieved significant accomplishments for all research goals of this project:

Goal 1: Develop crack geometry and mesh representation capability

1. We created a semi-automated, user-ready scripting interface between FRANC3D (geometric fracture representation code) and ExodusII (finite element database).
2. We demonstrated the ability to represent geometries of arbitrarily nonplanar cracks as they nucleate and propagate.
3. We demonstrated the ability to remesh for arbitrarily nonplanar crack evolution using linear, quadratic, or composite tetrahedral elements.

Goal 2: Model crack nucleation and propagation

1. We determined that Sandia's codes for mapping history-dependent analysis variables were not designed for the geometry adaptations and element types required by our crack modeling approach.
2. Since variable mapping is a necessity for our approach, we developed a new mapping code that addresses the complexities of geometrically modeling ductile fracture, e.g., sharp stress gradients and large deformations.

3. For the full suite of element types available to solid mechanics modelers at Sandia, we demonstrated our new code's ability to map fields and restart analyses for problems with element field gradients and large deformations.
4. We outlined future research and development activities intended for improving mapping capabilities, especially for accurate mapping of near-crack fields.
5. We extended and demonstrated the capabilities of the FRANC3D scripting interface to read displacement fields during an analysis so that crack tip displacements can be measured for the prediction of crack growth.
6. We modeled well-known crack growth patterns for tensile and shear loads in a pre-cracked, 3D plate, and we demonstrated the ability to represent cracks for a user application: fracture in glass-to-metal seals.

Significance:

For the science and engineering community, including the technical workforce, this project resulted in a fracture modeling capability that:

1. Reduces the dependence of crack paths on the numerics.
2. Leverages ongoing research in the fracture community, such as regularization methods and physics-informed damage modeling.
3. Encourages new research in related topics, such as variable mapping and geometrically explicit crack representation at multiple length scales.

This work supports the DOE national security mission to ensure the safety and integrity of nuclear weapons.

Clustered Void Growth in Ductile Metals 154568

Year 2 of 2

Principal Investigator: T. D. Kostka

Project Purpose:

Since ductile metals generally fail through the nucleation, growth and coalescence of voids, it is essential that we understand this phenomenon in order to better predict failure in these materials.

Using a developed research code, we are examining the problem of clustered void growth in ductile metals by investigating and identifying important microstructural configurations and attributes that accelerate or delay the formation and growth of voids and macroscopic material failure. In parallel to this, we wish to have these capabilities implemented into the SIERRA implicit dynamics code, Adagio. The first year of this project has been focused on researching clustered void growth with current capabilities and implementing the HEX20 element and a far-field traction-based boundary condition into SIERRA.

In the second year, we are able to validate the implemented features against analytical solutions and a current research code. We then transition away from the research code and explore clustered void growth for much larger problems by using parallel processing capabilities of SIERRA.

We will be creating a deeper understanding of clustered void growth under varying triaxiality, which will be instrumental in creating new void growth and predictive failure models. These results will be contrasted against those of dilute void growth to show the similarities and limitations of the dilute assumption.

Running large scale, representative three-dimensional clustered void growth simulations will put us at the forefront of modeling fracture surface.

Summary of Accomplishments:

1. We have performed a suite of tests looking at the effect of porosity on the macroscopic yield stress of the material in a plane strain framework. Results have shown the orientation of voids to have a large effect on the yield stress.
2. Preliminary simulations of a periodic 3D void microstructure are given along with the meshing procedure. Results show less void interaction as compared to the 2D case.
3. Development and implementation of an anisotropic plasticity model is detailed. The model is used to replicate anisotropic necking seen in a tensile bar experimentally tested to failure.
4. We have shown efficiency gains of 84% of a 2D solution framework compared the standard 3D framework.
5. We investigated a large number of element formulations and have shown the q1p0 element (selectively integrated hex8) to outperform all others in the context of large deformation plasticity simulations.
6. The implementation of the q1p0 element into SIERRA is provided along with results of verification and performance investigations.

Significance:

The void growth simulations allow the potential for improving our current void growth models to better replicate the response. Implementation of the q1p0 element enhances our predictive capabilities for ductile deformation. Development of the anisotropic plasticity model shows that we can model anisotropic response in ductile metals that we see in experimental results. Applications of this work potentially occur in the homeland security (DHS) area of infrastructure as well as in DOE low-carbon energy architectures such as in wind turbines.

Interface-Tracking Hydrodynamic Model for Droplet Electrocoalescence 155327

Year 2 of 3

Principal Investigator: L. C. Erickson

Project Purpose:

Many fluid-based technologies rely on electrical fields to control the motion of droplets (e.g., microfluidic devices for high-speed sorting of water droplets in oil or for purifying biodiesel fuel). Precise control over droplets is crucial for these applications. However, electric fields can induce complex and unpredictable fluid dynamics. For example, oppositely charged water drops immersed in silicon oil experience attractive forces that would favor their coalescence. Recent experiments with high-speed cameras demonstrate the counterintuitive behavior that these oppositely charged droplets bounce rather than coalesce in the presence of strong electric fields. A transient aqueous bridge forms between approaching drops prior to pinch-off. This observation applies to many types of fluids, but neither theory nor experiments have been able to offer a satisfactory explanation. Analytic hydrodynamic approximations for interfaces become invalid near coalescence; therefore, detailed numerical simulations are necessary. This is a computationally challenging problem that involves tracking a moving interface and solving complex multiphysics and multiscale dynamics, which are beyond the capabilities of present simulations. An interface-tracking model for electro-coalescence can provide a new perspective to a variety of applications in which interfacial physics are coupled with electrodynamics, including electro-osmosis, fabrication of microelectronics, fuel atomization, oil dehydration, nuclear waste reprocessing, and solution separation for chemical detectors.

Accurate and stable interface-tracking methods capable of capturing and predicting coalescence and break-up of interfaces are currently a major challenge in the computational science community. Including electric forces poses a further challenge due to the complexity of electrostatic and hydrodynamic interactions involved in coalescence, requiring a novel modeling approach to understand this phenomenon. This project will entail the creation of an interface-tracking model using the advantages of the Conformal Decomposition Finite Element Method with the capability to reproduce experiments, make predictions for future experiments, and answer questions about the physics of this phenomenon that are not experimentally accessible.

Automated Generation of Spatially Varying Stochastic Expansions for Embedded Uncertainty Quantification

155551

Year 2 of 3

Principal Investigator: E. C. Cyr

Project Purpose:

Uncertainty quantification (UQ) is increasingly recognized as necessary to assess the effect of variability of input parameters on a physical model. For phenomena described by systems of partial differential equations (PDEs), the variability is derived from coefficients, boundary conditions, or forcing terms, which are all modeled by a random variable with a particular distribution or a range of possible values. The result is a PDE that has a stochastic solution that reflects the variation in the input.

Current UQ methods like stochastic collocation or Monte-Carlo sampling approximate the stochastic solution by treating the required resolution of the uncertainty as uniform across the physical domain. To understand the consequence of this, consider a convection dominated flow where uncertainty is injected at a point in the domain. Only the solution downstream of the injection point will be affected by the uncertainty. The upstream solution will be fully defined by the deterministic PDE. Modern UQ methods would approximate both the upstream and downstream solutions with the same resolution. But, this wastes computational resources on the upstream solution and may under-resolve the solution downstream. For more realistic multiphysics applications that are characterized by a range of time and spatial scales, the required degree of resolution of the stochastic solution across the physical domain is an open question.

The research hypothesizes that the solution is more efficiently and accurately approximated by varying the resolution of the stochastic expansion across the spatial domain. Furthermore, using embedded UQ technology, the expansion can be constructed using adjoint-based error estimation and refinement. The potential benefit is two-fold. First, any investigation into the spatially varying resolution requirements of the stochastic solution represents novel research that will shed light on the nature of uncertainty in PDE systems. Second, an adaptive refinement algorithm would better utilize computational resources enabling simulation of larger, more complex physical systems, revealing greater insights into more challenging physics.

Softening Behavior of Post-Damage Quasi-Brittle Porous Materials 155798

Year 2 of 3

Principal Investigator: T. J. Fuller

Project Purpose:

The state of the art in structural failure modeling enables assessment of crack initiation and propagation, and progression to tearing, in many materials. Vulnerability assessments, and other applications (i.e., ceramic component manufacturing) suggest a need to track material behavior through failure, to the point of fragmentation and beyond. This field of research is made particularly challenging for structures made of porous quasi-brittle materials such as concrete, ceramics, rock, etc. These structures, when excessively loaded, will damage, soften, and eventually fail according to physical processes operating at comparatively large timescales in comparison to the initiating event. This project will develop constitutive models and associated numerical techniques suitable for capturing quasistatic softening, with experimental validation. This will be performed within the SIERRA Mechanics framework, but will be extensible to other formats.

The core of this research is the development of a softening model applicable to quasistatic loading that couples the constitutive response with that of the host finite element code by “shedding” load from highly stressed and softened elements to adjacent elements such that equilibrium is maintained at each load step, as required by the implicit solvers used in quasi-static analysis. The proposed stress shedding scheme has previously been attempted with some success in applications involving the softening of ductile materials, but has never been adapted to brittle materials. This method also differs from softening methods employed in explicit dynamic calculations in which softening is allowed to progress without respect to equilibrium. The challenge lies in the transition from an initial high-rate transient damage event (blast or impact) to more slowly evolving damage occurring over much longer timescales of interest in geomechanical analysis. Although this capability is potentially useful to many applications, it arises from a growing interest in blast and impact induced damage associated with DHS applications, as well as engineered subsurface reservoirs supporting future energy security.

New Methods of Uncertainty Quantification for Mixed Discrete-Continuous Variable Models

156158

Year 2 of 3

Principal Investigator: L. E. Bauman

Project Purpose:

The scale and complexity of problems such as designing power grids or planning for climate change is growing rapidly, driving the development of complicated computer models that incorporate both continuous and discrete data. Both the models and the data are uncertain. Uncertainty quantification (UQ) provides the underpinnings necessary to establish confidence in these models and their use to support risk-informed decision making. However, there are only a few approaches for mixed discrete-continuous variable models, and these become obsolete when there are multiple discrete variables or when the discrete variables are completely non-numeric. Therefore, researchers focus on the uncertainty in their particular problem taking advantage of symmetries, simplifications or structures. For example, uncertainty propagation in certain dynamical systems can be efficiently carried out after various decomposition steps. By combining some ideas from statistical genetics and computer experiments, we will develop a new method for performing UQ for mixed discrete-continuous models. We will focus on two general classes of problems: moderate scale problems (model choices) with a modest number of discrete variables and large-scale problems where the discrete parameter space may be larger than the continuous one (repeated units).

In classical biometrics when heritabilities are estimated, the aggregate effects of unobserved discrete genotypes are modeled as additive, continuous random variables. In computer experiments, one approach is to treat the deterministic output of a simulator as the sum of a fixed function and a random process. We will combine these approaches to create a new way to treat discrete variables in mixed variable problems. The key concept is to aggregate and transform the discrete variables into a continuous probabilistic variable, also leading to potential new capabilities for handling high dimensions.

This method will provide a new tool for UQ, which is focused on efficient estimation of the cumulative distribution function (cdf) of possible output function values given the uncertain input values.

Developing Highly Scalable Fluid Solvers for Enabling Multiphysics Simulation 156251

Year 2 of 3

Principal Investigator: J. Clausen

Project Purpose:

Computing hardware is trending towards distributed, massively parallel architectures in order to achieve high computational throughput. For example, Cielo will use 43,104 cores and Intrepid at Argonne National Laboratory uses 163,840 cores. Next-generation machines will continue this trend, with Sequoia at Lawrence Livermore National Laboratory using 1.6 million cores. This project is developing a fluid simulation algorithm based on artificial compressibility (AC) that is capable of scaling on massively parallel architectures.

Traditional incompressible-flow solvers are based on the incompressible Navier-Stokes (NS) equations, in which the continuity equation acts as a constraint imposing a divergence-free velocity field. In this case, no direct coupling of pressure to velocity exists requiring an implicit solution. The fully coupled finite element (FE) schemes currently used at Sandia scale to only $O(100)$ processor cores. As an alternative, fractional step (FS) methods such as the popular pressure correction method gain some scalability; however, they must still solve a Poisson equation for the pressure field, which creates a high communication load between processors resulting in poor scalability at $O(10,000)$ processors. An explicit FE method based on AC will allow for a local update procedure resulting in excellent scalability on $O(100,000)$ processors; however, as originally formulated, the AC method shows transient errors that must be addressed. The proposed solution uses a recently derived reformulation of the NS equations to eliminate these errors while retaining an explicit formulation.

Despite the uncertainties, the benefits of a scalable fluid solver will impact several areas at Sandia. This impact is most important in problems where high temporal resolution is required; for example, suspension and emulsion flows, thermal convective flows, melt flows, and fluid-structure interaction. If successful, this project will deliver a fluid solver capable of scaling with Sandia's increasingly parallel computational resources.

Simulation of Primary Fuel Atomization Processes at Subcritical Pressures 156703

Year 2 of 3

Principal Investigator: M. Arienti

Project Purpose:

The purpose of the project is to explore the fuel subcritical behavior in the liquid core and dense spray regions in injector devices. It is numerical in nature and provides an improved understanding of the very early stages of spray formation (primary atomization), as well as the capability to guide future experiments and diagnostics development by high-fidelity, high-performance simulations. Currently, external (with respect to the injection nozzle) simulations of primary atomization are carried out for the most part with simplified inlet conditions. Improving over this limitation, one of the major achievements in FY 2012 was to develop a simulation capability where internal and external flow are seamlessly calculated across the injection hole using the combined level-set volume-of-fluid (CLSVOF) method for the free liquid surface and a second level-set function ψ for the solid wall boundary. The computational mesh is Cartesian and block-structured; therefore, a grid cell belongs to the physical flow domain if $\psi > 0$. Cells that are near the wall boundary, but outside of the flow domain, form a narrow band of ghost cells where velocity boundary conditions are assigned. Assuming no cavitation, validation was carried out with an experiment using a scaled-up, transparent, six-hole Diesel nozzle where the velocity field was measured along the injection hole. Flow field features appearing just before the fuel exits into the combustion chamber could be highlighted, and their impact on spray characteristics was carefully studied. The same approach proved useful to simulate the motion of the injector needle — an essential element in understanding the transient dynamics of Diesel injection.

Multilevel Summation Methods for Efficient Evaluation of Long-Range Pairwise Interactions in Atomistic and Coarse-Grained Molecular Simulation

157688

Year 2 of 3

Principal Investigator: S. D. Bond

Project Purpose:

The availability of efficient algorithms for long-range pairwise interactions is central to the success of numerous applications, ranging in scale from atomic-level modeling of materials to astrophysics. Molecular dynamics (MD), in particular, can require months of supercomputer time, due to the expense of the large number of force evaluations required. The challenge is to design reliable, efficient, portable, scalable algorithms for calculating long-range interactions in large systems. Scalability and portability are of particular concern for modern exascale supercomputers with hybrid architectures and massive numbers of processors.

A diverse set of methods has evolved for rapid approximation of long-range interactions, including fast-multipole methods and Fourier-based particle-mesh Ewald methods. Multipole methods excel when applied to systems with large variations in density (e.g., astrophysics), but have generally been considered less competitive for more uniform systems (e.g., molecular dynamics). As a result, state-of-the-art MD codes like NAMD and LAMMPS, use particle-mesh Ewald.

Due to the use of the Fast Fourier Transform (FFT), particle-mesh Ewald methods do not scale well as the system size is increased, with a computational cost proportional to $N \log N$, where N is the number of atoms. The FFT also has a large communication overhead, due to the parallel scalability problems associated with the matrix transpose.

This project is focusing on the development and analysis of the multilevel summation method (MSM), which is a relatively new algorithm for computing pairwise interactions. Compared to particle-mesh Ewald methods, the MSM is lesser known, with the first MD studies appearing within the last five years. Preliminary studies have found that it has a computation cost proportional to N , rather than $N \log N$, and relatively low communication overhead (uses nested grids instead of the FFT). Development of this method has the potential to dramatically improve the efficiency of MD software used for predictive simulation of materials.

Predicting the Future Trajectory of Arctic Sea Ice: Reducing Uncertainty in High-Resolution Sea Ice Models

157957

Year 2 of 3

Principal Investigator: K. J. Peterson

Project Purpose:

The purpose of this project is to improve the fidelity of sea ice models and to develop methods to compare and propagate their uncertainties in order to provide new predictive capabilities for use in decision support.

Current generation Earth System Models (ESMs) vary greatly in their predictions for Arctic sea ice evolution, but all have underestimated the rate of decline in minimum sea ice extent over the last thirty years. Sea ice components of ESMs are multiphysics models with complex choices in the physical submodels and parameterizations used to define the governing equations and in the numerical methods used to discretize and solve the governing equations. They also contain many physical parameters with values that are inherently uncertain. A robust, predictive sea ice modeling capability requires an understanding of how uncertainties are propagated by different numerical algorithms and a consistent approach for comparative evaluation of the physical fidelity of each model.

We are employing a novel framework for calibrating and validating sea ice models using satellite and submarine data from the Arctic. The objective is to develop a systematic methodology to: 1) evaluate predictive capabilities of sea ice models, 2) discover the most important physical parameters contributing to uncertainties, and 3) assess the impact of numerical algorithms on sea ice simulations. Several sea ice models and model configurations are used to develop and test our approach. Alternative numerical implementations and physical models are being evaluated using the validation framework in order to determine the most relevant improvements. A distinguishing characteristic of the research is coordination of efforts in uncertainty/sensitivity analysis, physical modeling, and advances in numerical algorithms.

High Performance Graphics Processor-Based Computed Tomography Reconstruction Algorithms for Nuclear and other Large-Scale Applications 158182

Year 2 of 3

Principal Investigator: E. S. Jiménez, Jr.

Project Purpose:

The goal of this work is to develop a fast computed tomography (CT) reconstruction algorithm based on graphics processing units (GPU) that achieves significant improvement over traditional central processing unit (CPU)-based implementations. The main challenge in developing a CT algorithm that is capable of handling very large datasets is parallelizing the algorithm in such a way that data transfer does not hinder performance of the reconstruction algorithm.

General Purpose Graphics Processing (GPGPU) is a new technology that the S&T community is starting to adopt in many fields where CPU-based computing is the norm. GPGPU programming requires a new approach to algorithm development that utilizes massively multithreaded environments. Multithreaded algorithms are, in general, difficult to optimize since performance bottlenecks occur that are nonexistent in single-threaded algorithms such as memory latencies. If an efficient GPU-based CT reconstruction algorithm can be developed, computational times could be improved by a factor of 20. Additionally, cost benefits will be realized as commodity graphics hardware could potentially replace expensive supercomputers and high-end workstations.

Development of a fully optimized reconstruction algorithm may require a dramatic restructuring of the entire algorithm in order to achieve optimal performance. This project will take advantage of the CUDA programming environment and attempt to parallelize the task in such a way that multiple slices of the reconstruction volume are computed simultaneously. This work will also take advantage of the GPU memory by utilizing asynchronous memory transfers, GPU texture memory, and (when possible) pinned host memory so that the memory transfer bottleneck inherent to GPGPU is amortized. Additionally, this work will take advantage of GPU-specific hardware (i.e., fast texture memory, pixel-pipelines, hardware interpolators, and varying memory hierarchy) that will allow for additional performance improvements. At this time, the GPGPU algorithm technology is still in its infancy and development environments vary widely.

Sublinear Algorithms for Massive Data Sets

158477

Year 2 of 3

Principal Investigator: S. Comandur

Project Purpose:

Our ability to accumulate and store data is increasing rapidly. Increasingly, we are faced with massive data sets. These could be internet graphs, network traffic data, or genetic sequences of various organisms. Having gathered this data, we face the problem of processing it to learn something meaningful. In many cases, the data is too vast to complete even a single read pass through it. We need to develop sublinear algorithms (i.e., procedures that look at a tiny fraction of the data). The goal is to determine nontrivial properties of the data, such as recurring patterns in a string, sparse cuts in graphs, or communities in a cyber network.

These kinds of varied combinatorial and graph problems require very different kinds of sampling and algorithmic strategies. Over the past decade, the theoretical computer science and discrete mathematics communities have developed some algorithmic sampling tools for sublinear algorithms. This has yielded sampling procedures that are believed to be applicable for a large variety of problems.

This is an exciting and deep area of mathematical study, but most of the work has a very narrow, theoretical focus. The theoretical models are very rudimentary and many new ideas are needed to apply these sampling tools to specific problems. At a high level, our aim is to develop new theoretical sampling techniques and connect them to real-world issues at Sandia. This project promises to work both at the mathematical and practical levels. Any theoretical insights gained would be considered novel mathematical results in their own right. But understanding how these relate to real-world problems is uncharted territory in itself. This project would be one of the first comprehensive investigations in the study of sublinear algorithms for massive dataset problems.

Accurate Model Development for Large Eddy Simulation of Turbulent Compressible Flow Problems

158482

Year 2 of 3

Principal Investigator: M. Howard

Project Purpose:

Accurate simulation of turbulence is vital for predicting complex physical flow behaviors. Turbulence spans a large range of time and length scales and capturing all of its effects is difficult. Direct Numerical Simulation is too computationally intensive for high Reynolds number problems. Reynolds averaged Navier-Stokes simulations are less accurate and often inapplicable to many problems. Large Eddy Simulation (LES) resolves the predominant flow features and models the smaller scale turbulence. Of these approaches, it is clear that LES offers the best promise, but several significant challenges exist for compressible problems. Appropriate subgrid-scale modeling is an open area of research, especially for supersonic flows. Higher-order accurate numerical methods are essential to reducing discretization error. The interaction of the subgrid-scale model and the discretization method is also an important factor that is not fully understood. The investigation of these areas requires an efficient and scalable algorithm and poses significant challenges for accurately predicting complex turbulent compressible flows.

This research effort is motivated by the assertion is that a systematic investigation of unstructured discretization methods, filtering and subgrid-scale modeling techniques, and the interactions between the two, combined with a focus on accuracy and scalability, will enable a LES capability that surpasses existing limitations for solving turbulent compressible flow problems of national interest. We propose to rigorously identify the defining theoretical and numerical features of a successful LES scheme, and then develop a state-of-the-art capability for accurate unstructured LES of compressible flows. Two spatial discretization methods as well as implicit, explicit, and hybrid time integration techniques will be explored. This will enable us to make broad assessments about discretization characteristics that few existing research efforts have addressed. Determining the merits of each discretization feeds directly into investigating appropriate filtering techniques, subgrid-scale models, discretization errors and their interplay for this class of flows, all open and poorly understood topics.

Scheduling Irregular Algorithms

158787

Year 1 of 3

Principal Investigator: S. J. Plimpton

Project Purpose:

Scheduling is the assignment of tasks to processors for execution and it is an important concern in parallel programming. Most prior work on scheduling has focused either on static scheduling of applications where the dependence graph is known at compile time or on dynamic scheduling of independent loop iterations. However, many algorithms are irregular, which generally means that loop iterations are not independent and the dependence graph is not known at compile-time. In addition, scheduling traditionally focuses on improving locality or maintaining good load balance, but for irregular algorithms, even the amount of work may vary with the scheduling policy. The purpose of this project is to investigate novel strategies for partitioning the computations of a simulation into tasks that can be assigned dynamically to processors or processes or threads, so that irregular applications can run efficiently and scalably on thousands to millions of processors.

Irregular applications include traditional scientific applications (partial differential equations [PDEs], grids, particles), which are dynamic, either in their geometry or their time dependence. It also includes data-centric applications such as those in informatics or graph analysis where huge volumes of data are processed and the computation is often more memory-bound than compute-bound. High parallel performance for these kinds of applications is difficult for programmers to achieve due to load imbalances and the dynamic nature of the problems. As supercomputer architectures move to more processors and accelerated hardware such as many-core central processing units (CPUs) and graphics processing units (GPUs), the challenge is exacerbated. One possible solution is to automate more of the parallelization process by appealing to the compiler or a run-time system to partition a simulation's workload effectively and schedule the large number of small tasks on available resources (processes, threads, etc.). This project aims to extend the state of the art for that model, and apply it to interesting large-scale scientific applications. This work is in collaboration with the University of Texas-Austin.

Breaking Computational Barriers: Real-Time Analysis and Optimization with Large-Scale Nonlinear Models via Model Reduction

158789

Year 1 of 3

Principal Investigator: K. T. Carlberg

Project Purpose:

Despite developments in high-performance computing, high-fidelity physics-based simulations can take weeks to complete. This constitutes a barrier for many engineering applications. For example, uncertainty quantification (UQ) requires simulations to be completed in seconds or minutes; control requires real-time optimization using such models. For models with general nonlinearities, existing surrogate-modeling methods often fail to meet these time constraints without introducing unacceptable errors.

This project's purpose is to enable accurate, near-real-time analysis and optimization using high-fidelity physics-based nonlinear models via model reduction. The resulting framework will be generalizable and applicable to a wide range of problems including real-time control of power grids and UQ of thermal-mechanical systems. The work builds on the Gauss-Newton with Approximated Tensors (GNAT) model reduction method that has already generated exciting results for a wide variety of problems.

The PI is a President Harry S. Truman Fellow.

The project consists of three parts:

1. Integrate GNAT within a robust, predictive, model-reduction framework. First, decrease the temporal complexity of simulations. Second, devise error estimates/bounds for the solution. Third, investigate ways to refine the solution using error estimates. Task 1 is complete: we have submitted a journal paper.
2. Target applications: UQ and optimization. Each application carries unique requirements for the reduced-order model; the above framework will be specialized to these applications.
3. Deploy the model-reduction framework on problems of interest. First, devise strategies to preserve critical problem structure (e.g., energy conservation). Second, develop a single model-reduction software package that enables model-reduction for a wide range of problems. Third, investigate the effect of problem type and size on performance. We have implemented basic model-reduction capabilities in Albany, a computational mechanics code.

Exploring Heterogeneous Multicore Architectures for Advanced Embedded Uncertainty Quantification

158792

Year 1 of 3

Principal Investigator: E. T. Phipps

Project Purpose:

In the near future, high-performance computing will undergo dramatic changes as heterogeneous multicore nodes are incorporated into distributed memory architectures. Significant work is under way to exploit these new architectures for single-point forward simulations. However, critical to predictive simulation is the quantification of uncertainties in these simulations, for which propagation of uncertainties in simulation input data to simulation output quantities of interest is key. Since one avenue of forward uncertainty propagation relies solely on sampling a simulation code over the uncertain input space (so-called non-intrusive approaches) any improvement in the forward simulation enabled by multicore architectures will result in commensurate improvement in the forward uncertainty calculation. However, even with these improvements, there will be many problems of strategic interest where the computational requirements for accurate uncertainty propagation will still be too great. To address these challenges, it is critical to develop new architecture-aware uncertainty propagation algorithms that fully exploit the performance benefits of heterogeneous multicore architectures.

The purpose of this project is to create new embedded uncertainty quantification methods that fundamentally alter the structure of a simulation code to implement forward uncertainty propagation directly, leveraging high on-node core and thread counts, with the aim of achieving significant reductions in overall computational run times and increased scalability over non-intrusive methods. This requires fundamental algorithmic, computer science, and software research to develop algorithms and approaches that can leverage to the greatest extent possible the capabilities provided by these emerging architectures. Significant challenges are developing effective uncertainty-adapted solution strategies that scale to very high thread counts and software tools that allow these approaches to be incorporated in a diverse set of scientific simulation codes. The project's goals are foundational across all Sandia scientific computing missions, and it begins to illuminate a path to exascale computing where uncertainty quantification, not single-point forward simulation, is the driving technology.

Architecture- and Resource-Aware Partitioning and Mapping for Dynamic Applications

158793

Year 1 of 3

Principal Investigator: K. D. Devine

Project Purpose:

This project's purpose is the creation of new capabilities for distributing and mapping applications to processors in heterogeneous, dynamic, parallel computing environments. We are integrating real-time resource information with partitioning and mapping algorithms to dynamically assign and redistribute application data/work as computing-resource demands and availability change. An important step has been creating representations of target architectures compute hierarchy, network routing, and real-time performance.

- We wrote software to generate graph models of the NNSA's Alliance for Computing at Extreme Scale, Cray-XE6 Cielo network with accurate edge weights and exact static routing information. The generator works on any Cray-XE6 or XK6 (National Center for Supercomputing Applications' BlueWaters and Oak Ridge National Laboratory's Titan).
- We developed a node-subsystem representation of static and dynamic architecture information (static hierarchy from hwloc [portable hardware locality software package]); dynamic resource state from OVIS/LDMS). We will integrate this representation with network graphs in a complete machine representation.
- We developed low overhead data readers for performance events on the Cray-XE6 for non-intrusive collection of resource-utilization data, and tested them with linear-algebra kernels from DOE's FASTMath Institute.

Next, we sought effective mapping algorithms that account for applications' communication patterns in assigning processes to cores.

- We developed and simulated task-mapping algorithms to determine their effectivity in reducing average communication hops and execution time.
- We collaborated with the University of Illinois at Urbana-Champaign to extend the libtopomap library to use exact static routes and edge weights in mapping algorithms and congestion calculations.

We also developed software to integrate components for delivery to applications. We implemented software infrastructure for resource-aware dynamic partitioning, allowing Zoltan to use resource utilization data to determine part sizes.

Finally, we identified a target application to verify/validate our algorithms and software.

- We collaborated with Sandia's MiniGhost mini-application team to understand the effects of mapping, communication topology and link congestion on large-scale application performance.
- We are evaluating our data collection and mapping strategies in MiniGhost on Cielo in CCC3. Preliminary results show promise in reducing MiniGhost execution time.

Automated Algorithms for Achieving Quantum-Level Accuracy in Atomistic Simulations

158794

Year 1 of 3

Principal Investigator: A. P. Thompson

Project Purpose:

Molecular dynamics (MD) is a powerful materials science simulation tool for bridging between quantum mechanical (QM) systems with a few hundred atoms, and the length/time scales required to model entire microscale devices. However, the impact of MD is severely limited by the lack of suitably accurate interatomic potentials for many important materials. Examples include III-V semiconductor compounds such as indium phosphide and refractory metal alloys such as tantalum/tungsten. Building traditional physics-based potentials is a time-consuming, high-risk endeavor, incompatible with time-sensitive, mission-critical projects. A recent breakthrough enables automated development of quantum-accurate potentials for metals and semiconductor compounds with systematically controllable accuracy. This game-changing capability for predictive materials modeling may enable timely MD simulation of materials of arbitrary chemical composition with unprecedented fidelity, limited only by the availability of relevant QM training data.

The Gaussian-approximation potential (GAP) approach of Bartók et al. demonstrated that the bispectrum coefficients extracted from the projection of neighbor density on to the three-sphere can produce accurate regression surrogates for QM models. Using the GAP bispectrum formalism, we are building an in-house capability for automated generation of potentials for arbitrary materials using existing DAKOTA code regression tools coupled to the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD code. Specific to Sandia needs, we are generating potentials for refractory metals and III-V semiconductors. We are also creating a scalable parallel implementation of these potentials in LAMMPS, suitable for use in large-scale simulations. The primary risk we anticipate is whether these potentials can provide QM surrogates of sufficient accuracy for Sandia mission needs.

Electromagnetic Extended Finite Elements for High-Fidelity Multimaterial Problems

158795

Year 1 of 3

Principal Investigator: C. Siefert

Project Purpose:

The purpose of this project is to develop methods for computational modeling of electromagnetic (EM) surface effects in the case where body-fitted meshes are impractical. Modeling surface effects is critical, since current tends to concentrate near material surfaces. Many EM applications of interest to Sandia and Sandia customers operate in the large deformation regime, where body-fitted meshes are impractical and multimaterial elements are the only feasible option.

State-of-the-art methods use various mixture models to approximate the physics of these elements. The empirical nature of these models can significantly compromise the accuracy of the simulation in this very important surface region. Our approach is to develop an alternative simulation methodology to empirical mixture models for material surfaces.

Highly accurate, edge-based (compatible) discretizations form the basis for EM simulations at the NNSA labs, as they correctly respect the underlying physics. Unfortunately, there is no edge-based method that allows for resolution of sub-element material interfaces. Our goal is to build a physically realistic EM scheme that resolves these critical sub-element material surfaces. We are adapting ideas from the eXtended Finite Element Method (XFEM) to edge-based discretizations. The XFEM makes discontinuities at a sub-element level possible, but has only been developed for nodal discretizations. Realizing our goal requires the development of: 1) a novel edge-based technique to enforce the appropriate continuity conditions across material boundaries within an element, 2) implementation of the technique, 3) a novel, fully implicit linear solver capability to solve the resulting equations, and 4) a novel way to preserve XFEM quantities through large deformations (remap).

Ultrafast Laser Diagnostics for Energetic-Material Ignition Mechanisms: Tools for Physics-Based Model Development

158801

Year 1 of 3

Principal Investigator: S. P. Kearney

Project Purpose:

Despite its importance, a fundamental description of initiation in energetic materials has eluded researchers for decades, in large part because ignition results from mechanical and thermochemical mechanisms that are tightly coupled at extreme spatial and temporal scales of order microns and picoseconds. Access to these extreme time and length scales under dynamic loading conditions has, until recently, been restricted to simulations, and experiments to underpin the relevant physics are sorely needed to provide model developers with an appropriate physical foundation. The recent availability of femtosecond laser sources has opened the door to fundamental experiments with the required extreme resolution and well-controlled measurements on the early time effects of shock drive have been reported. These experiments have largely been limited to homogeneous materials, while the majority of explosives of interest — both ideal and improvised — are heterogeneous in composition, with material microstructure effects that are absent in homogeneous samples, but which can dominate the response in many real explosives.

We propose two significant leaps forward: 1) We will develop new capabilities for controlled small-scale shock-drive experiments on heterogeneous samples. Extension to these more challenging materials will additionally require us to 2) develop state-of-the-art ultrafast laser-diagnostic approaches for spatially correlated imaging and spectroscopy on a single-laser-shot basis with extreme picosecond- and micron-scale resolutions. We will advance the science of ultrafast imaging and spectroscopy to provide game-changing diagnostics for elucidation of the mechanical and thermochemical response of energetics to shock drive in well-controlled experiments on dynamically loaded heterogeneous materials. The measurements will provide new physical insight into the initiation process and provide fundamental data of interest to molecular-dynamics and mesoscale modelers. More significantly, the capabilities developed here will yield the first resolved-scale measurements of mesoscale phenomena, which will enable significant breakthroughs in modeling of shock propagation and ignition of more abundant heterogeneous explosives.

Fault Survivability of Lightweight Operating Systems for Exascale **158802**

Year 1 of 3

Principal Investigator: K. B. Ferreira

Project Purpose:

Concern is growing in the high-performance computing (HPC) community on the reliability of proposed exascale systems. Research at Sandia has shown that the reliability requirements of these machines will greatly reduce their scalability. Current fault-tolerance techniques have focused on application faults and ignored the most critical software running on a node, the operating and runtime system.

We can think of the operating system (OS) on these machines as a single, scalable application that manages the available resources on a node. Today's OSs and runtime systems make many of the same assumptions about reliability that applications do. Many of these basic assumptions will need to be addressed to enable more reliable system software.

HPC system software needs to be able to continue running through faults if emergent application-level fault tolerance is to succeed. This is in contrast to current OSs, which are unable to recover from the vast majority of failures. We will examine the structure of modern HPC OSs with the goal of characterizing important reliability assumptions and determining alternative strategies for exascale systems. For example, errors in memory and logic can have different impacts on the OS and a cost/benefit model for different approaches to handling such errors will need to be developed and analyzed.

In contrast to current fault-tolerance methods that are focused on application faults, this work is focused on developing operating and runtime systems that can continue in the presence of faults. This is a much finer-grained and dynamic method of fault-tolerance than the current, coarse-grained, application-centric methods. Handling faults at this level has the potential to greatly reduce overheads. Additionally, in contrast to much of the current work, this work focuses on more realistic faults, such as, silent data corruption. Lastly, in this project, we investigate forward recovery methods rather than the expensive rollback methods of current work.

Effect of Varying Convection on Dendrite Morphology and Macrosegregation 158803

Year 1 of 3

Principal Investigator: J. D. Madison

Project Purpose:

This work is a collaboration with the University of Arizona as well as Cleveland State University and is being established to: 1) understand the effects of melt convection and shrinkage flow on dendritic microstructure and 2) examine alloy macrosegregation during directional solidification. Microstructural morphology determines important macroscopic properties, therefore, enhanced control of microstructures are of economic importance in directionally solidified castings used in aerospace, power generation, and other industries. Initially, research will examine microstructural changes caused by varying thermal gradients and differing solidification rates under both microgravity and normal gravitational conditions. We anticipate that samples solidified under microgravity will produce microstructures practically free from the influences of convection, providing control cases in which the influence of convection can be reduced, if not eliminated, experimentally and subsequently modeled. Latter research will focus on the effects of changing cross-sectional sample area and the resulting changes in convection, shrinkage flows, and microstructural morphologies. These experiments will be carried out under normal gravitational conditions, and pending funding, under microgravity. The alloys used in these experiments will be Al-Si and Al-Cu, both of which are of commercial importance.

The novel approach here is in the attempt to grow relatively large samples of dendritic alloy, free from the effects of convection with minimized shrinkage flows, and characterize them by 3D reconstruction for comparison against gravitationally processed samples. In addition to characterization, experimental results will be compared to established solidification models with and without convective effects. This work is additionally innovative in that tools will be developed for furthering these types of investigations, such as techniques for the automated extraction of composition and morphology from micrograph images, direct comparison of solidification models with experiment, and the extraction of convection- and shrinkage-induced melt velocities as well as the quantifying and isolating other convective effects that would be otherwise unattainable.

Next-Generation Algorithms for Assessing Infrastructure Vulnerability and Optimizing System Resilience

158804

Year 1 of 3

Principal Investigator: M. Ehlen

Project Purpose:

The US economy and way of life are increasingly dependent on complex, adaptive, networked systems. These systems arise in critical infrastructure (e.g., electricity and water systems, transportation, banking and finance), global trade and supply chains, etc. Thus, understanding their behaviors under attack or disruption and increasing their resilience is an important national security challenge. A key component of these systems, which must be accounted for in vulnerability analysis, is their intelligent management by human system operators. Under attack, these actions ideally mitigate (though sometimes exacerbate) the system's response and also influence the subsequent behavior of the attacker.

The theme of this project, a collaboration with the University of Florida, involves bi-level discrete optimization problems for network design and security. Bi-level optimization problems involve two entities that make decisions in a non-cooperative fashion, often involving one primary entity whose actions are opposed by an adversarial entity. While contemporary mathematical programming techniques have been studied for simple cases, the methods cannot yet be extended to complex adversary actions or arbitrarily deep chains of operator/adversary interactions. This research seeks to develop new mathematical theory and algorithms in these areas.

If the research is successful, it will greatly expand the class of bi-level optimization problems that can be addressed with modern computational tools, and can be applied to varied national security mission areas including enhancing understanding of US critical infrastructure systems. Given that both foundational mathematical theories and practical implementations applicable to real-world problems do not yet exist, this project will create the scientific basis and demonstrate feasibility of an approach that could be differentiating to Sandia's national security missions and customers.

Next-Generation Suspension Dynamics Algorithms 158805

Year 1 of 3

Principal Investigator: P. R. Schunk

Project Purpose:

The goal of this project is to develop, refine, and apply next-generation algorithms for the simulation of dense suspensions of colloidal particles from the nanoscale through micron-sized particles. The challenge is to conduct mesoscale simulations for tracking the motion and self-assembly of individual nanoparticles while accurately accounting for hydrodynamic interactions, stochastic Brownian forces and interparticle forces. The algorithms must be scalable with $O(Np)$ ops to facilitate large-scale simulations over time scales (1 to 100 seconds) associated with colloidal diffusion, self-assembly, phase changes, and densification processing. To resolve the relevant physics requires large system sizes in terms of particle number with monodisperse suspensions of spheres requiring $O(10^3)$ particles and polydisperse suspensions, requiring much larger particle counts. To meet these needs, we developed the FLD (fast lubrication dynamics) algorithm, which demonstrated excellent predictions of physical phenomena while offering superior computational speed relative to ASD (accelerated Stokesian Dynamics), DPD (dissipative particle dynamics) and SRD (stochastic rotation dynamics). During the past year, we have further advanced the performance of the FLD approach by restructuring the algorithm from large sparse matrix formulations to denser, more compact near neighbor particle pairs data structures, and have reformulated the stochastic Brownian force computation for greater efficiency. Overall, this accelerates the parallel implementation and reduces bandwidth for data transfer.

With a high-performance FLD algorithm with proper verification and validation and scalability to large-scale computational clusters at Sandia, we will have a powerful tool for the analysis and development of novel nanostructured materials. These algorithms, capable of tracking the dynamics of self-assembly and guided assembly of nanoparticle structures, provide an invaluable tool in developing synthesis strategies for novel nanomaterials. These materials are at the heart of numerous laboratory thrusts to address national needs.

Multiscale Modeling of Brittle Heterogeneous Materials 158806

Year 1 of 3

Principal Investigator: T. Vogler

Project Purpose:

Heterogeneities and the mechanisms governing deformation in engineering materials often exist at length scales much finer than the engineering scale. Concrete is a good example. It possesses heterogeneities over many length scales while engineering structures are on the scale of meters. The scale of reinforcing phases such as aggregate and steel fibers is typically termed the mesoscale in concrete. Modeling at this scale is a methodology for understanding the role of microstructure during deformation, fracture, and failure. This scale is of particular interest due to the interfacial transition zone that exists between the cementitious matrix and the reinforcement, which typically acts as a crack nucleation point.

Peridynamics, a reformulation of continuum mechanics in integral form, is used to capture plasticity, strain softening, and fracture of bulk phases. Peridynamics offers two distinct advantages over classical continuum models, which rely on local balance laws. First, peridynamics does not rely on derivatives of the displacement field; thus, the discontinuities inherent to cracks can be included in a mathematically consistent manner. Second, as a nonlocal theory it is well suited to problems involving localization of plastic deformation and strain softening.

In this project, a collaboration with Georgia Institute of Technology, we are studying the behavior and failure of ultrahigh-performance concrete (UHPC) under high-rate impact and penetration using a multiscale approach capturing fine-scale deformation mechanisms to generate more accurate engineering-scale computations. Fine sand aggregate, steel fibers, and porosity will be explicitly modeled at the mesoscale in UHPC. The effect of reinforcement size and volume fraction will be determined and optimal material configurations determined. The work will serve as a basis for the development of new modeling and multiscale materials design approaches in the future. This problem has not been solved by current S&T due to both the computational demand and lack of appropriate constitutive theories to accurately address the problem.

Heterogeneous Scalable Framework for Multiphase Flows 158997

Year 2 of 3

Principal Investigator: K. V. Morris

Project Purpose:

Computational modeling of turbulent combustion is vital for our energy infrastructure and offers the means to develop, test and optimize fuels and engine configurations. In the case of internal combustion engines, fuel injection simulations provide insight into the required calibration for appropriate turbulent mixing and efficient combustion. In modeling the dilute spray regime, away from the injection site and downstream of the atomization processes, considerable doubts persist regarding how to best parameterize and predict the various two-way couplings between the dispersed phase and the surrounding fluid turbulence. These couplings include mass, momentum, and energy exchanges.

Two categories of challenges confront the developer of computational spray models: those related to the computation and those related to the physics. Regarding the computation, the trend towards heterogeneous, multi- and many-core platforms will require considerable reengineering of codes written for a specific supercomputing platform. Regarding the physics, accurate methods for transferring mass, momentum and energy from the dispersed phase onto the carrier fluid grid have so far eluded modelers. Significant challenges also lie at the intersection between these two categories. To be competitive, any physics model must be expressible in a parallel algorithm that performs well on multiple computer platforms.

To exploit the countless computing hardware configurations available and confront the challenges regarding portability and performance optimization for current scientific applications, the proposed work will develop a novel software architecture that segregates the data computation and communication from the physical models. This architecture will enable computational scientists to increase the versatility of present and future scientific codes. Current state-of-the-art spray model computations predict experimental results only for a narrow band of particle length and timescales. This work will simultaneously address a fundamental need to generalize these models to account for a wider range of particle scales, focusing on particles larger than the smallest turbulent eddies.

Interaction-Driven Learning Approaches to Complex Systems Modeling 159005

Year 2 of 3

Principal Investigator: A. V. Outkin

Project Purpose:

Combining interaction-driven and machine learning models into one cohesive framework will allow Sandia to develop complex systems models that will adapt in real time the model parameters and structure while harnessing the predictive power inherent to interaction-driven models. It will place Sandia in a leading role to provide decision support in areas such as response to natural or man-made disasters, sensor data processing, and cybersecurity.

Current progress summary:

1. Developed an initial conceptual framework. Investigated the applicability of the Statistical Learning Theory, and connections to the sensor networks.
2. Identified an existing interaction-driven model and a public data set for early testing of the framework.
3. Investigated the applicability of different learning algorithms and identified the Support Vector Machines — motivated approaches and conformal predictors as most promising tools. The currently implemented framework uses much simplified linear regression-based approach in order to quickly validate the feasibility of this method.
4. Created an initial software implementation using an existing interaction-driven model and a publicly available dataset and developed a set of Python, Tcl/Tk and R scripts for training and testing the prototype-learning model.
5. Tested the ability to run the interaction-driven model on a high-performance computer cluster to allow a more thorough investigation of the model parameter space and of applicable learning algorithms.
6. Conducted thousands of the interaction-driven model runs and demonstrated the feasibility of imitating the performance of a real-world system using only partially calibrated interaction-driven models.
7. Began development of collaborations with Rutgers University and Tokyo University.

Transactions for Resilience and Consistency in Integrated Application Workflows for High-Performance Computing

159006

Year 2 of 3

Principal Investigator: G. F. Lofstead

Project Purpose:

The scientific discovery process often involves a series of steps that may include simulation, analysis, and visualization with intermediate results staged on the storage system. For large-scale applications, the time, space, and power overhead of storing transient data is already overwhelming and will increase as machines and applications continue to increase in scale. Given these challenges, there is tremendous benefit in coupling these steps as an “integrated application workflow” (IAW). This approach eliminates storing transient data on the storage system but introduces new challenges with respect to resilience and data consistency.

For Sandia’s CTH shock physics code, understanding dynamics of material fragments, fragment tracking, is key for scientific insights. Generating fragment information requires separate analysis on the raw CTH data at every time step. An IAW for fragment detection eliminates the need to persistently store intermediate results making tracking fragments practical. Resilience is imperative because a failure or data corruption anywhere in the IAW invalidates the result.

Dramatic changes in data management must be made to achieve exascale computations. IAWs represent a fundamental change in the way computational science leads to insight; however, without resilience, IAWs are not practical at scale. A transaction-based technique provides a robust and scalable solution to resilience for IAWs.

Traditional distribution transaction management systems focus on a single client with multiple servers (1-N). For the high-performance computing (HPC) environment, however, there are potentially millions of clients interacting with thousands of servers (M-N). Collective input/output (IO) is an existing M-N style operation for HPC. To reduce the number of small IO operations, an initial phase rearranges data across the M processes before writing to N storage targets. The extreme overhead at scale shows what not to do while giving hints on how to manage some of the tasks, such as identifying the group of processes as a whole and the total amount and distribution of data.

Solution Methods for Network-Based Scheduling Problems

159054

Year 1 of 3

Principal Investigator: J. J. Carlson

Project Purpose:

The purpose of this research is to develop solution techniques for the new class of network-based scheduling problems. Motivating applications for this problem class include infrastructure restoration after an extreme event and plug-in hybrid electric vehicle (PHEV) battery charging and discharging within a smart grid. Infrastructures, such as power grids and transportation systems, can be modeled as networks. Network managers must coordinate repairs or operational decisions using limited resources in order to maximize performance. Selecting which components to repair or utilize (downed power lines, batteries to charge/discharge) can be viewed as network design decisions. Traditional network design decisions only focus on the end performance of the design (i.e., the network operation after all components are repaired). Clearly, in infrastructure restoration the success of the efforts depend on how well the services come back online. Therefore, it is important to allocate resources, such as work groups, to implement network design decisions. This resource allocation can be viewed as scheduling decisions. This novel model incorporating the combination of decisions occurring simultaneously does increase the problem difficulty, which motivates the need for both exact and approximate solution methods. In collaboration with Rensselaer Polytechnic Institute, we will adapt these methods in situations where not all information (components that need repair, battery demand) is available at the start.

Extensive research has been conducted in network design and scheduling separately. However, limited research has been conducted for the combination of these problems, denoted network-based scheduling. This problem integration captures the resource allocation aspects of network design, such as the time required to construct or repair networks and how the design influences network function over time. This novel way of modeling allows for many areas of exploration, but due to the increased problem difficulty, it calls for creative solution techniques that ensure an appropriate solution is attained within a reasonable amount of time to aid system managers.

Monte Carlo Processor Modeling 161139

Year 1 of 2

Principal Investigator: E. DeBenedictis

Project Purpose:

Our collaborator, Presidential Early Career Award for Scientists and Engineers (PECASE) recipient Jeanine Cook of New Mexico State University, has been developing a Monte Carlo-based processor modeling (MCPM) technique that can be used for performance analysis and prediction of contemporary and future processor architectures. These models abstract the execution pipeline into a stochastic model using both processor and application characteristics. Currently, both in-order and out-of-order execution and multi-core architecture can be modeled. We are pursuing new and continued work in three areas: 1) development of the MCPM technique to enable out-of-order, multi-core processor modeling, 2) MCPM integration within Sandia Structural Toolkit (SST), and 3) Mantevo benchmark performance analysis and validation.

SST is a system-level, parallel simulator that supports component models at varying levels of abstraction. We propose to fully integrate the stochastic processor models into the new stable core of SST. In some cases this includes developing front-ends to support various Internet Security and Acceleration (ISA) servers, including instruction decode and functional execution.

The Mantevo benchmarks were developed from key applications at Sandia and are intended to be short-running kernels representative of these applications. We propose a performance analysis at the architecture and microarchitecture level that will provide a detailed picture of benchmark behavior. With Sandia personnel, we will validate this data against each of the original applications from which these benchmarks were derived.

The complexity of contemporary and future computer processors has changed the methodology and tools that have been traditionally used for performance and design space analysis. Cycle-by-cycle simulation is very accurate and robust, but prohibitively slow, with slowdowns on the order of 10^4 . Therefore, new techniques and tools must be developed for the design and analysis of processors and processor systems. Further, the integration work will contribute processor models of an abstraction level that are currently not available in SST. Finally, the work on the Mantevo benchmarks will provide a much-needed validation at the microarchitecture level.

A Micro-to-Macro Approach to Polymer Matrix Composites Damage Modeling 161865

Year 1 of 3

Principal Investigator: S. A. English

Project Purpose:

Traditionally, polymer matrix composites (PMC) damage is assessed on the lamina scale in which distributed loads among the constituents exceed some failure criteria and lead to a reduction in laminate stiffness. An array of methodologies has been proposed to simulate this phenomenon. No consensus yet exists on the correct method to model damage and failure in composites. A micromechanical approach uses fiber and matrix properties to define decomposed constituent-level damage evolution and failure and thus may be extended to more complex compositions. Similarly, mesoscale (yarn) models can be used to directly assess damage evolution and failure in woven PMCs. The purpose of the project is to develop and implement a composites damage material model that uses a micro- and mesomechanical approach to determine homogenized macroscopic material response for varying levels of constituent complexity. Intermediate challenges include: implementation and evaluation of multiple material models, development of methodologies and length scale estimations for micro- and mesomechanical modeling, comparison with existing models (analytical and empirical) and experimental validation for simplified cases with materials of interest. Sandia's high performance computational capabilities allow for a detailed analysis of the microstructure, iterative optimization of material parameter selection and other tasks not generally suited for industry.

Digital Holography for Quantification of Fragment Size and Velocity from High Weber Number Impacts

161867

Year 1 of 3

Principal Investigator: D. R. Guildenbecher

Project Purpose:

In transportation accidents, tanks containing flammable or hazardous liquids may impact rigid surfaces at high velocity. This can lead to liquid dispersion throughout large volumes. In these situations, knowledge of the initial fragment sizes and velocities is needed to elucidate the fundamental physics and provide boundary conditions for predictive models of dispersion. Previous attempts to acquire such data were unsuccessful due to the spatial limitations of phase Doppler anemometry, which records droplets at a point, and particle tracking velocimetry, which records droplets in a 2D plane. To enable measurement of droplet statistics, innovative new methods are required to probe a large 3D domain in single-shot, short-duration experiments.

Significant advancement of the state of the art is proposed through the optimization of digital holography for quantification of the size, morphology, and velocity of liquid structures within a 3D measurement domain. The viability of digital holography has recently been established by a few proof-of-concept investigations and we propose three significant leaps forward for diagnostics for high-velocity droplet fields. First, we will greatly improve temporal resolution through the use of nano and picosecond laser pulses. Second, we will develop advanced algorithms to detect individual droplets and track them through multiple exposures. Finally, we will explore tomographic methods to improve the out-of-plane resolution of large-scale flow fields. Application of these techniques to high-Weber number impacts will provide new physical insights into the governing mechanisms and fundamental data of interest to multi-phase flow modelers. This data will enable significant breakthroughs in the development and validation of liquid dispersion simulations. Finally, once perfected, this technique could be extended to many other systems where index of refraction variation leads to light scattering. Consequently, the future application of digital holography may prove game changing for diagnostics of complex, 3D phenomena.

Aerosol Aging Processes and their Relevance to Human and Environmental Hazards

161873

Year 1 of 3

Principal Investigator: J. Santarpia

Project Purpose:

To understand the fate of any aerosol in the atmosphere and assess the impacts or hazards they pose, the atmospheric processes that affect the physical, chemical, and biological properties of airborne particulate matter must be characterized. For instance, the viability/toxicity and the fluorescence of chemical and biological warfare (CBW) agents and simulants released into the open atmosphere decay at vastly different rates as compared to those enclosed in conventional laboratory apparatus due to atmospheric chemical interactions and compounds, termed open-air factors (OAF). Because CBW agents cannot be studied outside, there are very few open-air decay rates to inform operational hazard prediction models. Further, there is little understood about the effects of OAF on the biological detection signatures for agents. Past and current studies indicate that the specifics of how long a biological attack may be detectable by current technologies are presently unknown. Tracers used to simulate the transport of CBW agents, and validate models, often rely on ultraviolet (UV) light induced fluorescence (LIF) for detection. The fluorophores in the tracer material may also be subject to the same degradation processes that affect CBW agents and stimulants. Finally, the radiative and hygroscopic properties of both anthropogenic and naturally occurring super-micron aerosol particles (such as dusts and bacteria) are critically important to understanding earth's climate processes. Laboratory measurements of these properties after known aging processes are relatively nonexistent.

This work proposes to develop new methods to study these complex problems and provide new information to inform a wide range of problems, including hazard prediction from weapons of mass destruction (WMD) and climate. These results should help enable the predictive capabilities of these fields. These problems represent significant gaps in chemical and biological hazard assessment that have had limited, if any, study.

Advanced Diagnostics for High-Pressure Spray Combustion 164668

Year 1 of 3

Principal Investigator: S. A. Skeen

Project Purpose:

Predictive high-pressure spray combustion simulations under development at Sandia will enable more rapid and cost-effective engine design that leverages fundamental physical and chemical information to reduce pollutant emissions and maximize efficiency. Anticipated advancements are crucial to the transportation sector as more stringent emissions regulations are imposed and new synthetic and bio-derived fuels with varying properties find greater usage. Development of a predictive simulation capability requires experimental data to both inform and validate the models, but very limited information is presently available about the chemical structure of high-pressure spray flames under engine-relevant conditions. Probing such flames for chemical information using non-intrusive optical methods or intrusive sampling techniques, however, is challenging because of the physical and optical harshness of the environment. For example, such flames are characterized by high velocities, temperatures, and pressures that make intrusive probing difficult. Further, beam steering effects caused by refractive index gradients are exacerbated at high pressure, complicating optical diagnostics. And finally, engine-relevant injection times are only a few milliseconds resulting in very small time-windows for measurements under quasi-steady conditions.

This experimental project will address the need for quantitative species information from high-pressure spray flames under engine-relevant conditions by developing and applying a suite of diagnostics to the constant volume high-pressure spray flame chamber at the Combustion Research Facility. The cutting-edge nature of the work lies in the development of a multiwavelength time-division multiplexed (TDM) absorption setup capable of providing temporally resolved species and temperature information at very short timescales. In addition, we will apply optical diagnostics and develop novel sampling techniques to investigate the chemical structure of high-pressure spray flames under conditions previously unexplored by these methods. The potential exists to acquire high-impact, quantitative data; however, there are many risks and challenges associated with the proposed diagnostics at high pressure.

Reduced-Order Modeling for Prediction and Control of Large-Scale Systems 164678

Year 1 of 3

Principal Investigator: I. Kalashnikova

Project Purpose:

Numerous modern-day engineering problems require the simulation of complex systems possessing many unknowns. Despite improved computational tools, “high-fidelity” models are often too computationally expensive for use in a design setting. The continuing push to incorporate into modeling efforts the quantification of uncertainties, critical to many Sandia applications, can present an intractable computational burden due to the high-dimensional systems that arise.

The proposed research aims to enable real-time simulations of complex systems for on-the-spot decision-making and control through the development of stable and efficient reduced order models (ROMs): models that capture the essential physics of interest at a low computational cost. For many ROM approaches, general results regarding the models’ fundamental mathematical properties are lacking, or the reduction is computationally intractable for large-scale problems. The proposed research will employ a provably stable and computationally tractable ROM technique as a starting point to explore methods for developing stable and efficient ROMs for the control of large-scale systems. The work can be seen as the first step towards the development of an effective model reduction technique to support decision-making under uncertainty. Targeted applications include the quantification of the captive-carry environment for the design of nuclear weapon systems, and atmospheric transport/climate modeling.

For a ROM to serve as a useful predictive tool, the model should preserve the stability properties of the original system and be cost-effective for large problems. As many ROM techniques are computationally intractable for large-scale systems or lack an a priori stability guarantee, there is motivation to explore new theoretically sound and computationally efficient techniques for building ROMs.

NANOSCIENCE TO MICROSYSTEMS INVESTMENT AREA

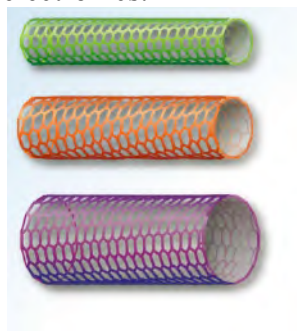
This investment area (IA) funds both fundamental and applied research into phenomena that arise from the distinctive properties of matter at the nanoscale (billionths of a meter), the scale of single atoms, small clusters of atoms, and small molecules, and of structures at the microscale (millionths of a meter). This includes both inorganic nanoparticle research and applications, for example, single atomic nanoparticles of metals such as gold, and also biological nanoparticles and nanomachines — and often, the combination of inorganic and biological, with bio-nanostructures sometimes providing models for developers to emulate.

Applications range from micromachines such as tiny heat engines and microelectromechanical systems (MEMs), to quantum cascade lasers to improved computer memories and new types of computing data structures (as in quantum computing), as well as nano- and microstructures showing novel optical and electromagnetic properties that tend not to be observed at larger scales. In addition to fundamental insights into the nature of materials and nanostructures, this IA ultimately offers solutions to problems in energy security, climate change, secure communications, cryptography, remote sensing and threat detection, and other arenas germane to national and global security.

Chirality-Controlled Growth of Single-Walled Carbon Nanotubes Project 141513

Single-walled nanotubes (SWNTs) consist of a single rolled sheet of graphene; rolling along different lattice vector lines produces SWNTs with differing chirality and diameter, each with its own unique electrical properties (including bandgap). All known synthetic methods produce SWNTs in mixtures of semiconducting and conducting types. Most methodologies to separate the different chiralities use post-growth separation methods. However these methods do not address how specific bandgap semiconducting nanotubes can be placed onto a microchip for next-generation electronics. Hence, this project has sought to develop CNT growth methods that will effect such differentiation.

Nanopore zeolite and anodized alumina oxide—/atomic layer deposition—based membranes have been synthesized as scaffolds for SWNT growth — templates providing precise steric limitations to within tenths of angstroms for SWNT diameters. Moreover, a growth technique has been developed enabling SWNT growth on silicon substrates previously coated with a tungsten barrier layer prior to nickel catalyst deposition. This new SWNT growth technique enables growth at temperatures as low as 350 °C, which is one of the world's lowest demonstrated growth temperatures for the production of SWNTs. Finally, a technique has been developed that enables the creation of free standing ordered nanoporous membranes with aspect ratios of greater than 10,000 to 1. These membranes have many potential uses including growth templates for SWNTs, ultimately enabling smaller, ultralow power electronics.

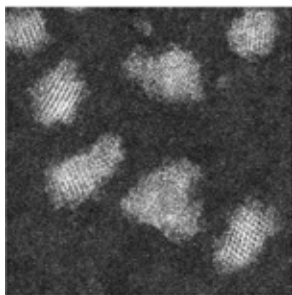


Drawing of carbon nanotubes with slightly different chiralities and electronic properties.

Development of Electron Nano-Probe Technique for Structural Analysis of Nanoparticles and Amorphous Thin Films Project 141514



This project is developing methodologies to analyze the atomic-level structure of very small nanoparticles utilizing Sandia's aberration corrected scanning transmission electron microscope. By collecting electron scattering data in scanning transmission mode, applying two transmission electron microscope (TEM)-based pair distribution functions and using a multivariate statistical analysis (MVSA) to analyze the datasets, the project has been able to determine bonding structure in "ultra" nanomaterials (UNMs) less than 5 nanometers in size. The method has been applied, for example to Li insertion into $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, nanomaterials important to battery research.



Above: Sandia's aberration-corrected scanning transmission electron microscope.
Right nanoparticle image.

Nanoscience to Microsystems Investment Area

Responsive Nanocomposites

141076

Year 4 of 4*

Principal Investigator: T. J. Boyle

Project Purpose:

The creation of environmentally responsive nanocomposites will result in materials which are much more robust and stable. To produce such nanocomposites requires that the surface interaction between functionalized nanoparticles and the matrix be better understood and controlled. This project will attack this pre-competitive general problem by invoking a multidisciplinary approach based on predictive computational models and experimental verification using a series of well-controlled complex nanomaterials dispersed in a variety of elastomeric or soft materials. We will determine the proper chemical species and length of the functional groups and the required surface coverage density of morphologically and compositionally varied nanomaterials dispersed in these matrices. Our initial response stimuli will focus on temperature or hydration since these are two of the major issues identified by our industrial (Goodyear, Exxon and Intel) partners. The project builds on Sandia's expertise in the synthesis of size- and shape-controlled nanomaterials of varied compositions and functionalizations, nanocomposite self-assembly, and computational modeling of nanocomposites aided by several key universities (Columbia, Cornell, Florida, Harvard, New Mexico, Northwestern, Texas, Washington) professors, students, and industrial partners with expertise in nanocomposite testing. Together, a model for nanocomposite mixtures that possess active or applied responses to temperature or hydration environmental changes is being developed.

Summary of Accomplishments:

Generated a wide variety of nanoparticles

- Established baseline electrospinning processes of variety of polymers
- Established nanocomposite baseline for reactive polymers
- Developed responsive nanopolymer wires
- Changed surface chemistry by including nanoparticles

Soft Templating Nanosynthesis

- Developed pH-responsive membranes using poly-4-vinyl pyridine
- Demonstrated pH-dependent hydraulic permeability
- Polymer can tunably reject solute particles

Interfacial Assemblies

- "Direct Writing and Actuation of 3D-Patterned Hydrogel Pads on Micropillar Supports" recently accepted for publication in *Angewandte Chemie Int. Ed.*
- Developed new method for patterning platinum and palladium with multiphoton lithography

Graphene Functionalization

- Developed new aerosol through plasma (ATP) synthetic method for disordered graphene
- Prepared new UV-photo-responsive, self-assembled reduced graphene oxide-TiO₂ nanometer films

* This 36-month project spanned four fiscal years

- Prepared AuTiO₂ core-shell nanoparticles to extend photo-response to visible wavelengths

Computational Calculations

- Modeled amorphous silica physisorbed with Si(OH)₃(CH₂)_nCH₃ (n=9, 17 and 35) alkylsilanes in alkanes of varying length
- Simulated the assembly of Au nanoparticles at water/vapor interface
- Determined forces between polymer-grafted nanoparticles in a polymer melt
- Carried out nonequilibrium molecular dynamics simulations to determine dependence of the shear viscosity on nanoparticle size and interaction strength

Significance:

This project employs a multidisciplinary research group consisting of national laboratory and university personnel that are developing a fundamental science concerning responsive nanocomposites. Students are involved in every aspect of this project. The project will allow for materials that can adapt to ever-changing conditions. This will revolutionize the packaging industry, materials durability, and flexibility for a single component — for example, a tire that can adjust to the weather, significantly improving safety, energy, and durability of tires, thus addressing transportation-energy goals of DOE. The project will also potentially address a wide range of other DOE applications, with an emphasis on energy-related needs.

Refereed Communications:

J.R. Potts, O. Shankar, L. Du, and R.S. Ruoff, "Processing-Morphology-Property Relationships and Composite Theory Analysis of Reduced Graphene Oxide/Natural Rubber Nanocomposites," *Macromolecules*, vol. 45, pp. 6045-6055, July 2012.

X. Xiao, T.E. Beechem, M.T. Brumbach, T.N. Lambert, D.J. Davis, J.R. Michael, C.M. Washburn, J. Wang, S.M. Brozik, D.R. Wheeler, D.B. Burckel, and R. Polsky, "Lithographically Defined Three-Dimensional Graphene Structures," *ACS Nano*, vol. 6, pp. 3573-3579, March 2012.

D. Meng, S.K. Kumar, J. Matthew, D. Lane, and G.S. Grest, "Effective Interactions between Grafted Nanoparticles in a Polymer Matrix," *Soft Matter*, vol. 8, pp. 5002-5010, February 2012.

C.E. Ashley, E.C. Carnes, K.E. Epler, D.P. Padilla, G.K. Phillips, R.E. Castillo, D.C. Wilkinson, B.S. Wilkinson, C.A. Burgard, R.M. Kalinich, J.L. Townson, B. Chackerian, C.L. Willman, D.S. Peabody, W. Wharton, and C.J. Brinker, "Delivery of Small Interfering RNA by Peptide-Targeted Mesoporous Silica Nanoparticle-Supported Lipid Bilayers," *ACS Nano*, vol. 6, pp. 2174-2188, February 2012.

L.D. Zarzar, B.S. Swartzentruber, J.C. Harper, D.R. Dunphy, C.J. Brinker, J. Aizenberg, and B. Kaehr, "Multiphoton Lithography of Nanocrystalline Platinum and Palladium for Site-Specific Catalysis in 3D Microenvironments," *Journal of the American Chemical Society*, vol. 134, pp. 4007-4010, February 2012.

L.D. Zarzar, P. Kim, M. Kolle, C.J. Brinker, J. Aizenberg, and B. Kaehr, "Direct Writing and Actuation of Three-Dimensionally Patterned Hydrogel Pads on Micropillar Supports," *Angewandte Chemie International Edition*, vol. 50, pp. 9356-9360, September 2011.

Calculations of Charge Carrier Mobility and Development of a New Class of Radiation Sensors for Real-Time 3D Source Location

141512

Year 3 of 3

Principal Investigator: M. S. Derzon

Project Purpose:

For national security reasons, a critical need exists to rapidly identify and locate ionizing radiation sources. The long-term goal is to pursue technologies that may one day lead to the manufacture of detectors of the same scale as traditional detectors but divided into a large number of micro-sized voxels (volume pixels with sizes of 50–700 microns). We estimate that such detectors with associated electronics and analysis software will greatly decrease the time to detect, identify, and locate a radioactive source compared with traditional radiation detectors. This benefit arises because each voxel gathers independent geometrical and timing information as if it were a single detector. Software tools enable the assembly of the geometric information. Timing information benefits from each voxel being very small. The extracted current from the slower carrier contributes less and less as the voxel size is reduced because the likelihood of another radiation event in a particular voxel becomes unlikely.

Because both Compton and photoelectric events contribute to the useful signal, the convergence in angle can be very rapid. These devices will not require external apertures (which reduce signal strength), and the whole cross-sectional area contributes to the sensitivity (unlike traditional Compton cameras that have a central spectrometer and external coincidence sensors). These will operate at room temperature and low power. In summary, the central hypothesis of this project is that it may be possible to monolithically fabricate a 3D pixelated sensor. One primary goal of the project was to model, test and demonstrate the component technologies at a single pixel level, which has potential to be scaled to 3D devices. The second primary goal of the project was to model, test and demonstrate the component technologies at a single pixel level, which has potential to be scaled to fully 3D devices.

Summary of Accomplishments:

Over the course of this work, numerous invention disclosures were filed. These comprise direct relation to the project and spinoff concepts that are not directly related to this work. Another invention disclosure is being developed with summary aspects using the latest results. This technology could result in a watch-scale alpha, beta, gamma, and neutron discriminating detector that may be able to serve as medical dose of record, rate-meter. There have been three peer reviewed publications and two abstracts submitted to IEEE Nuclear Science Symposium.

This effort has resulted in interest by another Sandia organization, fielding of sensor elements on Hermes and the National Security Technologies, LLC (NSTec) dense plasma focus and there has been follow-on funding. We will continue to pursue the work in those contexts as well as with CRADA partners (e.g., Aquila and Boeing, with others also possibly explored). Aquila has expressed interest in pursuing joint work.

Significance:

This work supports Goal 3 of the DOE strategic plan. It directly supports DOE and Sandia mission needs in nuclear security through defense, and nonproliferation by providing improved methods for meeting the goals of rapid identification and location of ionizing x-ray and gamma sources for special nuclear material (SNM) detection, material holdup, and surveillance and dosimetry. Numerous benefits accrue by comparison to current detection technology for our DOE and national security missions in defense, counterproliferation, and weapons of mass destruction (WMD) detection. The work may also

enable fully 3D microelectronic devices for terrestrial and space-based missions. It also enhances workforce capabilities by providing state-of-the-art training and understanding of competitive technologies.

Chirality-Controlled Growth of Single-Walled Carbon Nanotubes

141513

Year 3 of 3

Principal Investigator: S. M. Dirk

Project Purpose:

Single wall carbon nanotubes (SWNT) may be the most promising material to achieve game-changing impacts for future nanosystems and computing in the next decade. Much of the excitement surrounding SWNTs is their ability to be either semiconducting or ballistic conductors based on their individual crystalline structure, or chirality. SWNTs consist of a single rolled sheet of graphene; rolling along different lattice vector lines produces SWNTs with differing chirality and diameter, each with its own unique electrical properties. All known synthetic methods produce SWNTs in mixtures of semiconducting and conducting types. Typical chemical vapor deposition (CVD) processes, such as the Rice University high pressure carbon monoxide (HiPCO) method, simultaneously produce 80 different SWNT chiralities, where 2/3 are semiconducting, each with a different bandgap. Great efforts have been made to produce SWNT batches that are primarily semiconducting with narrow chirality distributions, most using post-growth chemical separation techniques. Separation methods, however, do not address the manner in which SWNTs of a given chirality may be placed onto a microchip. Therefore, even a successful chemical isolation of a given SWNT chirality will be difficult to implement in next-generation nanoelectronics.

This project seeks to develop methods to grow SWNTs with a given chirality (or bandgap) directly on Si substrates exactly where they are needed, using a process that is ultimately compatible with microelectronics processing. We have pursued the hypothesis that appropriate control of the reaction conditions will change the growth of SWNTs from a kinetic to a thermodynamically controlled process, resulting in high yields of specific SWNT chiralities. In addition, we have studied the novel use of nanopore zeolite and anodized alumina oxide/atomic layer deposition-based scaffolds as templates for SWNT growth, templates that provide precise steric limitations to within tenths of angstroms for SWNT diameters. The resulting combination of these unique approaches may lead to the growth of specific chiral SWNTs with specific semiconducting bandgaps located at precisely the right location.

Summary of Accomplishments:

Several key demonstrations and scientific findings have occurred during this project, including the development of a method to produce freestanding membranes with regular arrays of nanopores. The technique enabled nanometer control of pore size and is very reproducible. No other research group has demonstrated the capability to fabricate this type of free-standing membrane. The process uses a combination of anodized aluminum oxide (AAO) and atomic layer deposition (ALD) to create the nanopore membranes. The membranes have many potential uses including growth templates for SWNTs and other nanowire materials, and various filtration systems for water and gases. In addition, we have synthesized zeolites including Mordenite Framework Inverted (MFI) type (0.55-nm pores) in addition to mesoporous silica (3–4-nm pores). We have developed a number of solution-based catalyst deposition processes. We have demonstrated a growth technique that enables SWNT growth on silicon substrates, which have been coated with a tungsten barrier layer prior to nickel catalyst deposition in order to prevent nickel silicide formation. The new SWNT growth technique enables growth at temperatures as low as 350 °C, which is very silicon fabrication facility friendly and also one of the world's lowest demonstrated growth temperatures for the production of SWNTs. Low-temperature growth (350–490 °C) provides some control of nanotube diameter; however, the control is not as great as the control observed at higher temperature (530–630 °C). We have initiated a collaboration with Los Alamos National Laboratory and gained access to equipment for the purpose of chirality determination.

We have also developed a new single element Raman thermometry (SERT) characterization capability within Sandia.

Significance:

Perhaps the greatest achievement of this project has been the development of a technique that enables the creation of free standing ordered nanoporous membranes with aspect ratios of greater than 10,000 to 1. These membranes have many potential uses including growth templates for SWNTs, which will enable smaller, ultra-low power electronics, the controlled formation of nanowire materials for sensor applications of interest to DHS and DoD, and various filtration systems for the purification of both water and gases.

Refereed Communications:

S.J. Limmer, W.G. Yelton, M.P. Siegal, J.L. Lensch-Falk, J. Pillars, and D.L. Medlin, "Electrochemical Deposition of $\text{Bi}_2(\text{Te,Se})_3$ Nanowire Arrays on Si," *Journal of Electrochemical Society*, vol. 159, pp. D235-D239, February 2012.

Development of Electron Nano-Probe Technique for Structural Analysis of Nanoparticles and Amorphous Thin Films

141514

Year 3 of 3

Principal Investigator: P. Lu

Project Purpose:

In this project, we are developing two transmission electron microscope (TEM)-based pair distribution function (PDF) methods to analyze the atomic-level structure of nanoparticles (NPs) (<5 nm, crystalline or amorphous) and amorphous thin films. NPs and amorphous thin films are of great interest for basic science and energy-related research at DOE. The lack of long-range order in these materials makes structural characterization techniques based on traditional electron, x-ray, or neutron diffraction no longer useful. The methods developed in this project are analogous to the two established PDF analysis techniques of x-ray or neutron scattering and extended x-ray absorption fine structure (EXAFS), but offer several key advantages, including high spatial resolution (<1 nm), structural mapping capability, limited demands on sample size and quantity, and readily available access using laboratory-scale equipment.

We have used several novel approaches in the project, which have allowed us to overcome technical difficulties associated with analyzing electron scattering data. These approaches include collecting spectrum-image (SI) electron scattering datasets in scanning TEM (STEM) mode, analyzing the datasets using a multivariate statistical analysis (MVSA) approach, and integrating molecular structural modeling with structure determination and refinement. Significant progress has been made in the last eighteen months, meeting and/or exceeding most of the technical milestones in our project. The focus of the next year's follow-on research will be on optimizing the techniques using a new STEM and applying these techniques to study fundamental materials phenomena such as crystal-amorphous transformations, phase segregation, and interfacial interactions in conductive metal oxides.

Summary of Accomplishments:

We have developed two electron nanoprobe-based scattering techniques in TEM to analyze PDF for determination of bonding structure in “ultra” nanomaterials (UNMs), (<5 nm diameter, crystalline or amorphous) and amorphous thin films. The electron based techniques offers high spatial resolution (<1 nm), with limited demands on materials (a few particles, a single thin film), and with readily available access to the researcher. Our first approach uses the electron nanoscattering pattern (NSP) in the diffraction plane to extract local bonding structures, analogues to x-ray/neutron-based PDF. Our second approach uses the electron scattering equivalent of extended x-ray absorption fine structure (EXAFS), electron extended energy loss fine structure (EXELFS) of electron energy loss spectroscopy (EELS). We demonstrated that both techniques were capable of PDF analysis for UNMs and amorphous materials.

In addition to developing the electron-based PDF technique, we have also developed a hybrid imaging/diffraction technique that allows structural mapping of nanomaterial composites using the PDF functions. Our technique combines well-developed spectral imaging methods, NSP PDF analysis, and the principal component analysis of the NSP scattering dataset and allows for the phase mapping of the composites that are structurally different but chemically identical or different (e.g., amorphous TiO₂ vs. NP TiO₂). Finally, the techniques developed in this project were applied to several Sandia projects such as study of Li insertion in γ -Fe₂O₃ nanoparticles for battery research. We were able to illustrate directly the atomic processes of Li insertion in γ -Fe₂O₃ using the techniques.

Significance:

The new technique, developed in this project is unique to Sandia, and provides an important capability to characterize NPs and amorphous materials, crucial for advancement of nanoscience research and technology development. This technique stands to impact nearly all fields that currently utilize or study nanomaterials chemistry. Research programs in NPs and amorphous thin films are closely related to applications in renewable energy sources, energy storage, and alternative fuel technologies. The technique directly addresses technical needs for these programs and therefore impacts DOE critical missions in Energy and Energy transport.

Refereed Communications:

B.D. Gauntt, P. Lu, L. Yan, and Q. Jia, "Atomic Resolution Imaging of SmMnO₃/LaAlO₃ Interfaces using AC-STEM," in *Proceedings of the Microscopy and Microanalysis*, 2012.

B.D. Gauntt, P. Lu, and E.D. Spörke, "Probing Short-Range Order in Gamma-Fe₂O₃ as a Function of Ce Addition," in *Proceedings of the Microscopy and Microanalysis*, 2012.

P. Kotula, and P. Lu, et al., "Progress with the Sandia Titan G2 80-200 with 0.7sr Integral SDD Array," in *Proceedings of Microscopy and Microanalysis*, 2012.

Dynamically and Continuously Tunable Infrared Photodetector using Carbon Nanotubes

141515

Year 3 of 3

Principal Investigator: F. Léonard

Project Purpose:

Infrared (IR) photodetectors play a key role across Sandia mission areas being used for example in space-based surveillance, thermal imaging, aerial surveillance, and nondestructive imaging of components. IR detectors rely on pixel arrays, each pixel having a dimension in the ten to twenty micron range. Pixels are often made of exotic semiconductors like $\text{Hg}_{(1-x)}\text{Cd}_x\text{Te}$ because the bandgap (and thus the sensitivity to different optical wavelengths) can be controlled by varying the composition x . However, once a composition is chosen, this fixes the sensitivity to a specific range of wavelengths leading to black-and-white detection. As everyday experience with human vision shows, color detection improves discrimination significantly, and the same applies to IR detectors. Thus, one important need is dynamic multiwavelength detection in the IR. Current technology achieves two-color detection at the pixel level using a triple layer thin film approach, where two films with different compositions contact a common electrode layer. Unfortunately, this does not provide an obvious path for continuous multi-wavelength detection. To address this issue, we propose to utilize the unique properties of carbon nanotubes (CNTs) to demonstrate an infrared pixel with continuously and dynamically tunable absorption. The concept relies on the fact that the bandgap of CNTs is sensitive to strain, with a change of 100 meV per percent strain, as demonstrated experimentally and theoretically. By fabricating a CNT nanoelectromechanical (NEM) device, we will control the strain applied to the CNTs and achieve tunability of the optical absorption. Such CNT NEMS have been demonstrated with resonant frequencies of tens of megahertz (MHz), and can thus be rapidly tuned. Our experimental work will be coupled with theory and modeling of the photophysics of strained CNT devices. Finally, we will test the radiation hardness of these devices.

Summary of Accomplishments:

We developed new theoretical approaches to calculate the electronic and optical properties of carbon nanotubes, and included the effects of doping and strain. We discovered unusually large bandgap renormalization due to doping, which can lead to the decrease of the bandgap by several hundred meVs. We also found that doping reduces the exciton binding energy by a large amount, but in a continuous fashion. These effects were explained by the presence of acoustic plasmons that change the electronic screening.

We developed novel approaches to fabricate supported and suspended carbon nanotube devices, and we measured their electronic and optoelectronic properties. We discovered unusual reverse and forward bias behavior under illumination.

We also tested the radiation hardness of nanotube devices by exposing them to gamma and proton irradiation. We found that the devices are very resistant to radiation, even at very large doses.

Significance:

The work in this project has shown that carbon nanotubes possess unique properties for optoelectronic devices. The combination of theory and experimental work has identified a number of very promising R&D areas that could lead to novel types of photodetectors. These photodetectors are critical to many national security missions, including space-based surveillance for DOE nonproliferation programs.

Refereed Communications:

C. Spataru and F. Léonard, “Tunable Exciton and Quasiparticle Properties in Doped Semiconducting Carbon Nanotubes made possible by Acoustic Plasmons,” to be published in *Chemical Physics*.

Efficient, High-Voltage, High-Impedance GaN/AlGaIn Power FET and Diode Switches

141517

Year 3 of 3

Principal Investigator: A. G. Baca

Project Purpose:

High-voltage solid-state power conversion technology is a key enabler for increasing the penetration of renewable-energy electricity sources by virtue of that technology's ability to enable a wide variety of power conversion needs: high-voltage DC transmission, DC/AC, AC/DC, or DC/DC conversion for transmission or distribution. Conventional solid-state power conversion either operates at insufficient voltage levels or, as in light-triggered thyristors, is costly, lacking sufficient ruggedness and efficiency to be widely deployed. Conventional bulk drift devices (e.g., Si thyristors) are sufficiently mature that theoretical and practical limits to breakdown, based on the minimum controllable doping level, have not significantly changed in 30 years. We propose to study and improve the lateral GaN/AlGaIn transistor because its conductive properties arise from charge polarization effects without intentional doping, and therefore, may have a considerably higher breakdown limit. The goal is to achieve breakdown beyond 20 kV. Such a goal does not lend itself to an engineering solution because the wide variety of device structures and material combinations that must be fabricated and tested at high voltages is uneconomical. Rather, a science-based approach is warranted—studying and understanding the effects of device design and material combinations on leakage currents that limit breakdown at <5 kV (wafer probe limit) to build a model that scales beyond 20 kV. The main technical challenges include the following: understanding the factors limiting breakdown field in these lateral devices, understanding the role of material, geometry, and voltage on leakage and peak electric fields, as well as the role of surface passivation.

Summary of Accomplishments:

We discovered a method to increase the average electric field in GaN/AlGaIn high electron mobility transistors (HEMTs) to twice the value previously achieved (and one-third of the theoretical value) through fundamental science methods (patentable). This work shows that the perceived sweet spot for GaN/AlGaIn HEMT breakdown voltage can be extended beyond 300-600 V.

We also discovered a new type of transistor with GaN/AlGaIn HEMTs utilizing the side gate. This side gate transistor exhibits the following benefits: large on-off current ratio, high transconductance (nearly equivalent to the conventional transistor), very low off-state leakage current, and very low subthreshold slope.

Significance:

This work extends the frontiers of engineering in high-voltage power electronic devices. If follow-on work is successfully realized, these results can enhance DOE/EERE's and Sandia's Energy Security mission by enabling greater penetration of renewable energies on to the electricity grid.

Electrodeposition of Scalable Nanostructured Thermoelectric Devices with High Efficiency

141518

Year 3 of 3

Principal Investigator: P. A. Sharma

Project Purpose:

Power generators and refrigerators based on the thermoelectric (TE) effect operate without moving parts, involve no liquid or gas medium, can be made compact, and are extremely reliable over long time periods. Despite these advantages and numerous potential applications, current TE devices have limited uses due to the low efficiency of present bulk materials. Nanostructured TEs have much higher efficiency but their limited dimensions and costly fabrication makes them useless for most applications. We seek to create a high-efficiency nanostructured TE material with bulk dimensions using electrodeposition, a scalable technique. Synthesis is rapid with deposition rates of microns per minute. Chemistry and microstructure can be reliably varied at the atomic scale by tuning deposition parameters.

While electrodeposited nanostructured TE materials have been demonstrated in the literature, no attempts have been made at scaling up a process to bulk dimensions. Our main challenge in this area will be to control nanostructure and chemistry while scaling our deposits to bulk dimensions. Since the TE properties of electrodeposits are unknown, we will focus on understanding the microstructure-property relations in electroplated thermoelectrics.

This project directly addresses a technology that could revolutionize refrigeration and power generation. Present nanostructured TEs are not only limited in scale, but also have, as reported in the literature, irreproducible properties due to uncontrolled microstructure and carrier doping. Our project focuses on these two roadblocks simultaneously because if we succeed in fabricating a bulk scale nanostructured TE, we will then be able to systematically study how nanostructure affects transport using more reliable bulk measurements.

Summary of Accomplishments:

We focused on two different nanostructures in the Bi_2Te_3 system shown to increase the thermoelectric figure of merit: 1) superlattices and 2) nanoparticles. We focused on Bi_2Te_3 -based structures, since these materials possess a high intrinsic $ZT \sim 1$ and are more commercially relevant. We reported three different approaches for forming these nanostructures: melt synthesis of naturally occurring $\text{Bi}_2\text{-Bi}_2\text{Te}_3$ superlattices, electrodeposition of $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$ superlattices, and surfactant-based, electroless synthesis of Bi_2Te_3 nanoparticles. We succeeded in forming 50-nm period multilayers using electrodeposition, achieving a nanoscale grain size in electrodeposited materials, and controlling the size and stoichiometry of Bi_2Te_3 nanoparticles. We discovered the origin of low thermal conductivity in $\text{Bi}_2\text{-Bi}_2\text{Te}_3$, and also found that this materials system becomes superconducting under large (GPa) pressures, where the superlattice structure is lost. We succeeded in scaling electrodeposits to a 200-micron thickness over a large (4-inch diameter) area. We demonstrated that roughness limits the ultimate thickness of electrodeposits.

Significance:

TE devices are used for power generation and solid-state refrigeration applications, and impact such areas as vehicle electrification, increasing detector sensitivity through spot cooling, nondestructive testing, biometrics, night-vision, and remote power sources. They are of interest to DOE/BES Physical Behavior of Materials Program, as illustrated by a recent Thermoelectricity workshop conducted by the Office of Science. These results may ultimately impact the development of thermoelectric systems for

several national security missions. The techniques we have developed should be useful for fabricating devices and for realizing materials with higher performance than has been achieved previously.

Refereed Communications:

J.L. Lensch-Falk, D. Banga, P.E. Hopkins, D.B. Robinson, V. Stavila, P.A. Sharma, and D.L. Medlin, "Electrodeposition and Characterization of Nano-Crystalline Antimony Telluride Thin Films," *Thin Solid Films*, vol. 520, pp. 6109-6117, January 2012.

D. Banga, J.L. Lensch-Falk, D.L. Medlin, V. Stavila, N.Y.C. Yang, D.B. Robinson, and P.A. Sharma, "Periodic Modulation of Sb Stoichiometry in $\text{Bi}_2\text{Te}_3/\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ Multilayers Using Pulsed Electrodeposition," *Crystal Growth and Design*, vol. 12, pp. 1347-1353, February 2012.

Greater Than 50% Efficient Photovoltaic Solar Cells 141519

Year 3 of 3

Principal Investigator: J. Wierer

Project Purpose:

We are developing a new photovoltaic (PV) cell structure that will allow solar power conversion of 50%. “Hero” monolithically grown laboratory cells have achieved ~43% efficiency. However, these cells have a number of constraints that limit efficiency, including lattice matched material requirements resulting in non-optimum bandgaps and inefficiencies in converting time-varying solar spectra from series connected cells. To exceed 50% efficiency, we will stack individually grown and connected junctions. This will avoid degradation due to lattice mismatch, reduce series resistance losses, allow ideal bandgaps for maximum efficiency, and eliminate current matching so the cell stack can operate well in any solar spectrum. Key ST&E challenges include development of materials and cells for junctions of the proper bandgaps, the heterogeneous integration of cells, and developing micro-concentrators. In parallel, we will also look at InGaN-GaN nanowire architectures that can absorb the entire solar spectrum.

To exceed 50% photovoltaic efficiency, we are creating a stacked structure of individually grown and contacted cells, avoiding lattice and current matching requirements. We will first develop a three-junction cell comprised of Si, GaAs, and InGaP. These junctions will be assembled within a receiver substrate and packaged with integrated concentrating optics, putting significant effort in developing the optical system to minimize optical losses in the cell stack and achieving efficiencies approaching 50%. Next, we will develop a four-to-five-junction cell of InGaAs, Si, GaAs, InGaP, and possibly InGaN. The development of the InGaN junction will require developing new growth techniques to achieve the desired bandgap using strain-relief structures and nanowire architectures. Finally, graded-InGaN/GaN core-shell nanowire structures will be developed that absorb the entire solar spectrum in a single junction.

Summary of Accomplishments:

A solar cell based on a III-nitride hybrid nanowire-film architecture was demonstrated. It consisted of a vertically aligned array of InGaN/GaN multi-quantum well core-shell nanowires, electrically connected by a coalesced p-type InGaN canopy layer. This hybrid structure allowed for standard planar device processing, solving an important challenge with nanowire device integration. It also enabled various advantages such as higher indium composition, InGaN layers via elastic strain relief, efficient carrier collection through thin layers, and enhanced absorption via nanophotonic light trapping. This proof-of-concept nanowire-based device presents a path forward for high-efficiency III-nitride solar cells. Fabricated III-nitride nanowire solar cells exhibited a photoresponse out to 2.1 eV and short circuit current density of ~1 mA/cm² (1 sun AM [air mass] 1.5 G [global]).

Significance:

This is a first demonstration of an III-nitride nanowire array solar cell, addressing the interests of DOE’s Energy Efficiency and Renewable Energy (EERE) program in photovoltaics. It shows a pathway forward for higher efficiency III-nitride nanowire solar cells. It has generated new intellectual property, and places Sandia in a position for similar follow on programs. This III-nitride nanowire accomplishment could be beneficial to Sandia within a 5–10 year timeframe.

Refereed Communications:

G.T. Wang, Q. Li, J.J. Wierer, J. Figiel, J.B. Wright, T.S. Luk, and I. Brener, “Top-Down Fabrication of GaN-Based Nanorod LEDs and Lasers,” in *Proceedings of SPIE 8278, Light-Emitting Diodes: Materials, Devices, and Applications for Solid State Lighting XVI*, 2012.

J.J. Wierer, Jr., Q. Li, D.D. Koleske, S.R. Lee, and G.T. Wang, “III-Nitride Core–Shell Nanowire Arrayed Solar Cells,” *Nanotechnology*, vol. 23, p. 194007, 2012.

Microfabricated Nitrogen-Phosphorus Detector: Chemically Mediated Thermionic Emission

141520

Year 3 of 3

Principal Investigator: R. J. Simonson

Project Purpose:

Selective ionization of organic molecules that contain group five heteroatoms occurs on or near the surface of thermionic emission cathodes. This phenomenon has been exploited for many years to make highly selective nitrogen-phosphorus detectors (NPDs) for hazardous gases. In spite of this long history, the details of this chemically mediated surface emission phenomenon are poorly understood. While the N- and P-sensitivity of such devices can exceed that for other hydrocarbons by 10,000X, the NPD signal current ultimately depends on the transfer of electrons across the surface potential barrier of the thermionic cathode (emitter). As military and homeland security needs drive requirements for smaller and more powerful detection technologies, operational problems, including limited source lifetime and high power consumption, become increasingly severe. This necessitates the development of a new micro-NPD. These devices will improve selectivity, speed, sensitivity, and portability of detectors for explosives, toxic industrial chemicals (TICs), and chemical warfare agents.

Two classes of competing mechanisms have been described in the literature to account for the chemically selective ionization observed in NPDs: 1) gas-phase ionization models and 2) surface mediated electron emission. The latter mechanism is considered more likely based on a review of the literature. In order to both investigate the proposed surface-mediated ionization mechanism and to improve performance of microfabricated NPDs, we conducted a systematic study of novel candidate thermionic emission materials. Efforts were primarily concentrated on sol-gel deposited alkali-doped high-porosity silicate films. The performance and stability of these cathode emitter films were measured by a combination of methods, including direct measurement of surface variations in work function of novel materials by scanning probe methods, systematic correlation of novel cathode material composition and microstructure with both work function and NPD performance, and the design and test of novel microfabricated cathode structures for micro-NPD applications.

Summary of Accomplishments:

Our team synthesized and characterized a novel set of Group I and II metal alkoxide precursor compounds as potential solution-phase dopants for sol-gel derived metal silicates. We also developed and tested two new designs for microfabricated heater substrates capable of operation in air at temperatures up to approximately 800 °C. These devices allowed us to test the thermionic sensor response of sol-gel derived cathode emitter films in atmosphere. Both the amplitude of sensor response and the selectivity of the thermionic emission current for different classes of organic vapors were measured.

Significance:

The selectivity of the microfabricated NPD detectors toward toxic vapors containing nitrogen, phosphorus, or halogen heteroatoms as compared to hydrocarbons has direct impact on the development of portable instrumentation for the detection and identification of chemical warfare agents as well as other compounds of interest to US government agencies, such as DHS and the defense threat reduction agency (DTRA). The national security missions of military force protection, weapons nonproliferation, and homeland security will, therefore, benefit from these results. DTRA has expressed interest in further development of this sensor technology.

Refereed Communications:

T.J. Boyle, L.A. Steele, A.M. Saad, M.A. Rodriguez, T.M. Alam, and S.K. McIntyre, "Structural Diversity in a Series of Alkyl-Substituted Cesium Aryloxides," *Inorganic Chemistry*, vol. 50, pp.10363-10370, October 2011.

T.J. Boyle, L.A. Steele, and A. Saad, "Synthesis and Characterization of the Heavy Alkaline Earth Aryloxide Cogeners," *Inorganica Chimica Acta*, vol. 394, pp. 259-268, January 2013.

Nanoporous Polymer Thin Films from Tri-Block Copolymers 141521

Year 3 of 3

Principal Investigator: J. G. Cordaro

Project Purpose:

Our goal in this project was to create new nanoporous polymer membranes by designing and making block copolymers that would self-assemble into thermodynamically favorable, ordered nanodomains suitable for chemical modification in order to control transmembrane transport properties. The project combined our expertise in polymer synthesis, computational modeling, fabrication and characterization of thin films, and membrane testing. Current membrane applications are limited by poor ion-selectivity, environmental conditions, difficult and expensive manufacturing techniques, ill-defined nanostructure, and weak mechanical properties. By controlling the morphology and pore selectivity on the nanoscale, many such limitations may be overcome. Furthermore, by decoupling the mechanical and chemical components of the membrane, improved performance, including longer lifetimes, greater specificity, and altogether novel behavior from these new membranes could be realized. Ultimately, robust thin-film polymer membranes with chemically tunable properties were the goal of this research.

Summary of Accomplishments:

Our efforts thus far have led to the development of computational method for predicting polymer morphology, the synthesis of numerous macroinitiators and block copolymers, and phase-identification of polymer thin-films using x-ray scattering techniques and electron microscopy.

- We demonstrated that triblock polymers could be synthesized in three steps from commercially available starting materials. These materials were not available at the onset of this project.
- We showed that triblock polymers could be functionalized, first with an azide and second with a pyrene dye, after performing a Huisgen cycloaddition reaction. This new polymer was characterized using nuclear magnetic resonance and ultraviolet visible (UV-Vis) spectroscopy and size-exclusion chromatography.
- We demonstrated that block polymers could be selectively deuterated using an iridium catalyst. This opens up the possibility of selectively enriching one microdomain of a polymer with deuterium, which will greatly improve the signal-to-noise in neutron scattering experiments.
- We discovered that re-initiation of nitroxide-mediated polymerization (NMP) macroinitiators under thermal polymerization conditions does not proceed as efficiently as needed to make triblock polymers.
- We built a model that shows that fast evaporation of solvent cast block polymer films yields perpendicular alignment of the morphology.
- We realized that small-angle x-ray scattering (SAXS) measurements using a 1D detector are of poor quality compared to a dedicated SAXS instrument, which is not available at Sandia.
- We characterized polymer thin films using three different instruments for comparison. From these studies we learned that a dedicated SAXS instrument is probably essential to performing proper and time-efficient characterization techniques of polymers.

Significance:

Our work has improved our capabilities in three core technical areas that align with the DOE mission of scientific discovery and innovation. First, our ability to synthesize and characterize polymers has been greatly enhanced over the course of this project. Second, we employed self-consistent field theory calculations to help model the phase behavior of block polymers. This approach will lead to a better understanding of polymer morphology and enable us to design better materials via tuning the structural-functional relationship. Third, we utilized high-energy particles (x-ray, neutrons, and electrons) to probe

the solid state structures of polymer films. This technique is critical for our understanding of materials properties, especially in aging.

Surface Engineering of Electrospun Fibers to Optimize Ion and Electron Transport in Li^+ Battery Cathodes

141522

Year 3 of 3

Principal Investigator: N. S. Bell

Project Purpose:

The purpose of this research is to understand and find a solution to degradation of a lithium-ion cathode material in order to improve lifetime cycling and reliability of batteries. We are investigating LiMn_2O_4 (spinel lithium manganese oxide [LMO]), a commonly researched cathode material. In practice, this material experiences several degradation mechanisms ranging from capacity fading, the Jahn-Teller distortion phenomenon leading to dissolution in the electrolyte phase, and the formation of surface films by degradation of the electrolyte, and/or phase transitions at the surface to form Mn_2O_3 .

This project is developing fiber synthesis techniques for the formation of the active material, and a continuous method for coating the core with a shell of protecting material to allow for stabilization of structural and electrochemical properties. Sol-gel chemistries for the synthesis of LMO and zirconia have been implemented to generate these fiber morphologies. The electrospinning process and the new force spinning process have been applied successfully to form these fibrous materials. Characterization of the cycling degradation of the core LMO phase has been studied using scanning tunnel microscopy (STM) of these fibers in electrolyte, on a gold-coated substrate. This provides the first direct evidence of processes occurring at the interface, such as dissolution of the active material, facet development, decomposition of the electrolyte to form a surface electrolyte interface (SEI) layer, or the formation of Li alcoxides/carboxylates. Computational modeling of the degradation of the battery electrolyte fluid over LMO surfaces has been initiated, and will extend to ceramic passivating materials as candidates for the protective shell oxide. The project is developing the knowledge of these materials so that the degradation mechanisms of the active energy-storage material can be understood and is also developing a protective interface that resists these processes through optimization to permit rapid Li^+ transport, good e-conductivity, a stable interface, and prevention of the solid-electrolyte interphase (SEI) layer.

Summary of Accomplishments:

In this project, we:

- developed novel techniques for forming fiber based, core-shell cathode materials,
- developed a new capability for in situ electrochemical study of the operational degradation of the cathode material, and
- calculated theoretical pathways for the decomposition of the lithium-ion battery electrolyte, as well as the dissolution of the manganese ion into the solvent, with reprecipitation as inactive material.

We directly observed the degradation mechanism in electrochemical cycling for the first time, and novel methods for forming core-shell cathode materials were developed and submitted for patent protection.

Significance:

The development of new techniques for in situ observation of material viability during electrochemical cycling adds a significant capability to Sandia research, as do new capabilities in fiber material processing, which can be extended to application across a wide class of materials (ceramics, metals, polymers) and applications, including energy storage, energy collection and transport, and thermal processing. Reflecting the DOE theme of scientific discovery and innovation, these developments will impact fundamental science in electronics, energy storage, composite materials, photovoltaics, catalysis, and materials processing.

Understanding the High Temperature Limit of THz Quantum Cascade Lasers (QCLs) Through Inverse Quantum Engineering (IQE) 141523

Year 3 of 3

Principal Investigator: I. Montano

Project Purpose:

This project will answer the following question: Is there a fundamental maximum operating temperature for Terahertz quantum cascade lasers (THz QCLs)? The answer will have significant impact on determining what applications THz QCLs can address. Although the maximum operation temperature increased rapidly after THz QCLs were first invented in 2001, there has been very little improvement over the past few years and the maximum operating temperature achieved (185 K) still requires cryocooling. The slow progress has led many to speculate that the maximum operating temperature is fundamentally limited by the ratio of the photon energy to the thermal energy in the system ($h\nu/kT > 1$). While much data seems to fit this theory, recent results have significantly weakened, perhaps even disconfirmed, the hypothesis and no good theories have yet replaced it. Many studies have explored how different design parameters affect laser performance, but with the existing techniques there has been limited direct connection between the studied parameters and the laser physics. This use of indirect measurements has resulted in a lack of systematic understanding. In this project, we are using the unique capabilities of our inverse-quantum-engineering (IQE) algorithm to systematically disentangle temperature-dependent, performance-limiting physics from the many interdependent material parameters of THz QCLs.

Summary of Accomplishments:

In this project, we showed that our IQE algorithm allows creation of model families of designs that isolate targeted experimental effects, thus allowing direct investigation of specific physical mechanisms and their often complicated and counterintuitive interplay.

We used IQE to design two sets of frequency-shifted THz QCL lasers (i.e., two families of lasers with all parameters identical except for the lasing frequency). By growing, fabricating, and measuring the set of lasers, we obtained experimental proof that our IQE algorithm is capable of successfully frequency-shifting a given THz QCL design. Furthermore, the sets of frequency-shifted lasers gave us unprecedented experimental access to a model system perfectly suited to isolate and directly investigate the impact of the laser frequency on laser performance. We showed that the maximum operating temperature depends more on the specifics of the design itself than on the actual lasing frequency. This experimental result not only questions the still widely believed hypothetical $h\nu/kT > 1$ limit, but furthermore, is a first important step in understanding the temperature dependence of THz QCLs.

With the goal to also investigate the temperature dependence theoretically, we additionally developed a k-resolved, fully microscopic, quantum kinetic performance simulator that takes into account carrier-field interactions, carrier-phonon interactions, carrier-impurity interactions, and carrier-carrier interactions including both diagonal and non-diagonal correlation contributions. Including numerically highly demanding features such as multisubband screening, the nonequilibrium phonon distribution, and scattering to energetically higher subbands, we were able to achieve excellent agreement with in-house measurements. We showed that the developed simulator, which in contrast to previously existing simulators does not depend on any fit parameters, correctly predicts the current density for a wide range of lattice temperatures and applied voltages. Initial theoretical results from studies investigating the impact of the laser frequency on laser performance are consistent with our experimental results showing the importance of design specifications.

Significance:

This project created deeper theoretical understanding of the interplay between physical mechanisms that control the behavior of complex heterostructure devices. The immediate impact addresses Sandia's interest in the physics of nanoscale structures and phenomena, as well as in tool development, and will have longer-term impact on microdevices and microsystems. The physics is relevant to many intersubband devices such as mid-infrared (MIR) QCLs, advanced MIR detectors, thermal-photovoltaics and thermal energy harvesting. These will impact many national security applications. Most specifically, the developed IQE design tool allows the design of THz QCLs for screening applications, component inspection, and molecular identification applications in support of the programs of agencies such as DHS and DTRA.

MBE Growth and Transport Properties of Carbon-Doped High-Mobility Two-Dimensional Hole Systems

141933

Year 3 of 3

Principal Investigator: J. L. Reno

Project Purpose:

This research, in collaboration with Purdue University, involves the study of molecular beam epitaxy (MBE) growth, device fabrication, and transport properties of 2D-hole systems (2DHS) in carbon doped GaAs heterostructures. The research will be of interest to a wide audience of researchers in physics, electrical engineering, and materials science, given that the project involves fundamental research in materials growth, novel devices in electronics and spintronics, as well as low-dimensional systems for use in fundamental physics research.

Historically, hole systems have not been as extensively studied as electron systems due to the lack of an ideal p-type dopant, which resulted in hole samples having a lower material quality than comparable electron systems. However, recent advances in the use of carbon as a p-type dopant have enabled the growth of hole systems that are of significantly increased quality. We are pursuing a systematic growth study of these hole systems to determine the fundamental limits of material quality, specifically hole mobility, of carbon doped GaAs quantum structures. This has both scientific and technological relevance. First, low-density hole systems simultaneously exhibit strong carrier-carrier interactions with strong spin-orbit coupling, which is of interest to physicists studying spin-related phenomena. Second, the lower hyperfine coupling of holes (as compared with electrons) to atomic nuclei is important for applications in spintronics and solid state quantum computation, both of which require spin systems that are decoupled from their environments.

Summary of Accomplishments:

Facilitation of the lab, set-up of vacuum systems for outgassing cells and gallium purification, installing and rendering operational a new MBE system, and set-up of a ^3He cryostat and a dilution refrigerator for sample characterization were accomplished.

- 2DHS have been grown and characterized that demonstrate fraction quantum Hall effect (FQHE) physics that is among the best in the world.
- It was found that, unlike electron mobility, hole mobility follows complicated density dependence due to the interplay of interface roughness scattering, remote impurity scattering, alloy scattering, and background impurity scattering.
- The maximum 2 DEG mobility achieved thus far: $22 \times 10^6 \text{ cm}^2/\text{V}\cdot\text{s}$.
- A record was set for largest energy gap (570 mK) of the $\nu = 5/2$ fractional quantum Hall state.

Significance:

Utilizing a new high mobility GaAs growth facility at the Birck Nanotechnology Center (BNC) at Purdue University, a systematic investigation of MBE growth of carbon-doped high mobility two-dimensional hole systems (2DHS) was performed. New physics and new device applications often follow from advances in material synthesis. The recent development of efficient resistive carbon doping filaments allow for the construction of extremely high quality two-dimensional hole systems on the high symmetry (100) face of GaAs. The initial studies focused on determining the parameters that presently limit low temperature mobility in carbon-doped 2DHS. These studies are relevant to DOE missions in both scientific discovery and innovation and in alternative energy technologies.

Refereed Communications:

N. Samkharadze, J.D. Watson, G. Gardner, M.J. Manfra, L.N. Pfeiffer, K.W. West, and G.A. Csathy, “Quantitative Analysis of the Disorder Broadening and the Intrinsic Gap for the $\nu = 5/2$ Fractional Quantum Hall State,” *Physical Review B*, vol. 84, p. 121305(R), September 2011.

A.T. Hatke, M.A. Zudov, J.D. Watson, and M.J. Manfra, “Magnetoplasmon Resonance in a Two-Dimensional Electron System Driven into a Zero-Resistance State,” *Physical Review B*, vol. 85, p. 121306(R), March 2012.

J.D. Watson, S. Mondal, G. Gardner, G.A. Csathy, and M.J. Manfra, “Exploration of the Limits to Mobility in Two-Dimensional Hole Systems in GaAs/AlGaAs Quantum Wells,” *Physical Review B*, vol. 85, p. 165301, March 2012.

J.D. Watson, S. Mondal, G.A. Csathy, M.J. Manfra, E.H. Hwang, S. Das Sarma, L.N. Pfeiffer, and K.W. West, “Scattering Mechanisms in a High-Mobility Low-Density Carbon-Doped (100) GaAs Two-Dimensional Hole System,” *Physical Review B*, vol. 83, p. 241305(R), 2011.

Metrology of 3D Nanostructures

142440

Year 3 of 3

Principal Investigator: R. Boye

Project Purpose:

The goal of this project is to develop techniques for the inspection of 3D nanostructures, in collaboration with University of Colorado-Boulder. Such structures are critical for novel nanomanufacturing with potential applications including metamaterials, volume optics, nanoelectromechanical systems, photonic crystals, optical circuits, and other devices that control light propagation at the micro- and nanoscale. However, better metrology methods are necessary to properly characterize and inspect these devices, particularly as these structures expand in volume and shrink in feature size. The feature sizes that can be fabricated are already several times smaller than the wavelength of visible light and are beyond the resolution limit of a standard microscope (scanning electron microscopes can be used to form high-resolution images, but are limited in terms of sample preparation, speed, and cost). Current super-resolution techniques are specifically tailored to biological applications. However, the methods will have to be adapted to solve the unique problems presented in materials metrology.

We are using quantum dots as the fluorescent emitters. Quantum dots have many unique optical properties that make them favorable choices as emitters, but the most significant difference compared to other emitters is their temporal characteristics. Due to the presence of trap states, the quantum dots randomly switch between bright and dark states. This blinking is typically viewed as a disadvantage; however, this property can be exploited as a contrast mechanism to differentiate between two closely spaced dots. Fortunately, many of these optical and computational techniques can be applied to a wide range of problems. Obviously, samples that do not emit their own light must be labeled with emitters. In other cases, the sample under test is already emitting light, and a system could be designed and constructed to exploit this emission to precisely determine the location of these objects in 3D. An example would be ions emitting at 397 nm in a surface ion trap setup.

Summary of Accomplishments:

We developed a super-resolution technique to resolve dense clusters of blinking emitters. The method relies on two basic assumptions: the emitters are statistically independent, and a model of the imaging system is known. We extended a current technique known as Independent Component Analysis (ICA) to allow for an unknown number of quantum dot emitters to be resolved. We numerically analyzed the performance limits of the method as a function of the emitter density and the noise level. Numerical simulations showed that five closely packed emitters can be resolved and localized to a precision of 17 nm. The experimental resolution of five quantum dots located within a diffraction-limited spot confirms the applicability of this approach.

Significance:

This project will advance the DOE's goal of improving nanophotonics technology by improving 3D inspection techniques. Sandia's expertise in creating large nanostructured samples requires matching techniques for inspection and metrology in 3D. Moreover, optical imaging with 3D super-resolution well beyond the wavelength of light has applications in medicine, biology, materials science, and nanofabrication inspection in both research and industrial settings.

Refereed Communications:

A.J. Barsic and R. Piestun, “Superresolution of Dense Quantum Dot Clusters using Independent Component Classification,” in *Proceedings of the Computational Optical Sensing and Imaging*, 2012.

Enabling Self-Powered Ferroelectric Nanosensors: Fundamental Science of Interfacial Effects under Extreme Conditions

142543

Year 3 of 3

Principal Investigator: J. Ihlefeld

Project Purpose:

Physically small and unobtrusive devices that can sense and report on their environment without relying on external power sources (batteries) would be of benefit to both US industry and DOE programs. Ferroelectrics are ideal candidate materials for compact sensors because their coupled electro-physical properties mean that they could potentially draw power (via piezoelectric energy harvesting) from the environments that they are sensing. Advances in fabrication have made possible the thought of economical nanosensors based on ferroelectrics. To be a viable technology, there are several challenges that must be addressed including: incomplete knowledge of the effects of corrosive environments on the materials used, radiation damage on material performance, and mechanisms controlling nanoscale interfacial microstructure and chemical homogeneity, which will impact performance. Knowledge is incomplete in many of these areas owing, in part, to limited tools to study these features and the lack of a cohesive team of diverse background to perform research. This project assembles such a team that is evaluating the intrinsic effects of aggressive environments on ferroelectric performance and ferroelectric-electrode interface integrity, factors that are critical to determining the feasibility of developing and deploying the envisioned self-powered sensors.

This project is developing and leveraging in situ characterization tools to understand ferroelectric material and interface degradation in real time. These real-time studies have not previously been performed on these complex materials systems and only through this kind of information can the mechanisms that affect ferroelectric performance be understood. Only through fundamental understanding of the mechanisms regulating material and interface degradation in aggressive environments can reliable devices be developed and deployed. This project is identifying these mechanisms and enabling development of a deployable nanosensor technology. We are collaborating with a team of university experts in corrosion, nuclear engineering, and ferroelectric structural characterization, their expert research complementing the ferroelectric synthesis and characterization expertise of Sandia.

Summary of Accomplishments:

- We have developed new in situ x-ray diffraction characterization techniques to monitor film phase assemblage and texture development during crystallization.
- We determined the sequence of phase formation in lead zirconate titanate (PZT) thin films on platinized silicon substrates during crystallization at multiple heating rates. We have identified the precursor phase to be pyrochlore and not fluorite, as has been reported by previous researchers.
- We have also shown that lead-platinum intermetallic phases do not appear to contribute to film texture; film heating rate and substrate metallization appear to have a strong influence on final film crystallization texture.
- We demonstrated a new substrate metallization technology that enables chemical gradient free films with improved ferroelectric performance.
- We developed a new scanning microdroplet electrochemistry analysis instrument to study electrochemistry of thin films.
- We developed the first known Pourbaix diagram for PZT.

- We have identified the role of film defects on the corrosion resistance of PZT films in sulfuric acid; elimination of defects is necessary to prevent film degradation.
- We have developed an understanding of the role of film stoichiometry on corrosion resistance to sulfuric acid environments: titanium-rich films are more resistant to degradation than zirconium-rich compositions.
- We have developed an understanding of the effect of initial film quality on its resistance to degradation in neutron radiation-rich environment: films with low leakage currents and well-defined polarization response are more resistant to degradation than films of lesser quality.

Significance:

The scientific understanding developed by Sandia and our university partners will substantially impact DOE, DHS, DoD, and other agencies interested in the future development of unobtrusive self-powering sensors. For example, knowing exactly how these nanoscale systems respond in a variety of radiation environments will assist with the evaluation of materials for satellite systems, as well as for potential unattended sensors to monitor the transport of illicit radioactive material. Furthermore, stability of such nanoscale materials systems in corrosive chemical environments, particularly those relevant to marine and/or petrochemical applications, will be of great interest to DoD as well as US industry.

Refereed Communications:

L. Small, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, "Electrochemical Response of Ferroelectric $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ Thin Films," *Journal of the Electrochemical Society*, vol.159, C357-C363, 2012.

L. Small, A. Cook, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, "An Automated Electrochemical Probe for Evaluation of Thin Films," *Journal of the Electrochemical Society*, vol. 159, F87-F90, 2012.

J.F. Ihlefeld and C.T. Shelton, "Chemical Homogeneity Effects on the Nonlinear Dielectric Response of Lead Zirconate Titanate Thin Films," *Applied Physics Letters*, vol. 101, p. 052902, July 2012.

C.T. Shelton, P.G. Kotula, G.L. Brennecka, P.G. Lam, K.E. Meyer, J-P. Maria, B.J. Gibbons, and J.F. Ihlefeld, "Chemically Homogeneous Complex Oxide Thin Films via Improved Substrate Metallization," *Advanced Functional Materials*, vol. 22, pp. 2295-2302, June 2012.

Integration of Block-Copolymer with Nanoimprint Lithography: Pushing the Boundaries of Emerging Nanopatterning Technology

145832

Year 3 of 3

Principal Investigator: G. L. Brenneka

Project Purpose:

The rapid pace of innovation enabling Moore's Law (doubling transistor density every ~1.5 years) is critical to our nation's technological leadership and economic security. To maintain this pace, the International Technology Roadmap for Semiconductors (ITRS) prescribes, by 2022, an 11-nm half-pitch for dense patterns and 4.5-nm critical dimensions. Current 193-nm immersion optical lithography can print ~40-nm half-pitch and may reach 20 nm with double patterning. Extreme ultraviolet (EUV) lithography persistently raises doubts due to the costly complete change of infrastructure. Therefore, alternative lithographic pathways to the extreme nanoscale ITRS goals are needed. In this project, we will direct the self-assembly of block copolymers (BCP) into device-oriented patterns fabricated by optical interference lithography (IL), use those self-assembled BCP patterns as masks to create nanoimprint lithography (NIL) masters via plasma etching, and fabricate prototype devices using this combined "top-down" and "bottom-up" approach.

BCP-based patterning techniques excel at extreme nanoscale feature definition but have significant limitations related to defect density, long range order, and the fabrication of multiple feature types on a single wafer. Using IL-directed BCP, we will achieve long range order across device-relevant dimensions, and by building up a single NIL master from multiple IL+BCP directed self-assembly (DSA) coupons, we will be able to fabricate essentially arbitrary patterns of extreme nanofeatures unencumbered by optical diffraction limitations. Extensive metrology associated with relevant characteristics (critical dimensions, line edge roughness, pattern fidelity, defect density and distribution, etc.) at every stage of the process will provide guidance about the eventual feasibility of this approach. This project is the first combination of IL with BCP and NIL technologies, and will define the limits of a combined top-down/bottom-up lithography approach for use in commercial applications including integrated circuit manufacture.

Summary of Accomplishments:

While we had difficulty integrating all aspects of the project into a single ideal process flow, a pair of proxy applications was selected to demonstrate the integration of pairs of the technologies.

Wire grid polarizers (WGP) for use at ultraviolet (UV) wavelengths were demonstrated using interference lithography on fused silica and Al evaporation. Even though the microscopic structure of the initial WGP samples were suboptimal, we were still able to achieve extinction ratios between the allowed/rejected polarization of >100 from the mid-UV (300 nm) out through the visible, demonstrating the potential of this approach.

Block copolymer-defined features of ~20nm were transferred into Si for nanoimprinting, then the residual poly(methyl methacrylate) (PMMA) layer at the bottom of the holes was removed by an oxygen plasma inductively-coupled reactive ion etch. One nm of Cr and 5 nm of Au were e-beam evaporated onto the imprinted substrate, followed by liftoff to leave behind Au nanodots which were successfully demonstrated as effective substrates for surface enhanced Raman scattering (SERS) using Rhodamine 6G (R6G) molecules adsorbed onto the device surface. Initial results show varying defects and imperfections that resulted from each pattern transfer step, but even the imperfect features produced several orders of magnitude enhancement in Raman scattering response.

We were able to bring some level of block copolymer directed self-assembly capabilities to Sandia and demonstrated the first-ever integration of interferometric lithography with the directed self-assembly of block copolymers. We also developed in-house recipes for etching of tiny features in unusual materials and bilayers, and our University of Wisconsin collaborators were able to demonstrate the critical importance of surfaces during direct self-assembly of block copolymers via coupled experiment and simulation.

Significance:

Demonstration of the integration of interferometric lithography and directed self-assembly of block copolymers was an important technological step forward, and the large number of publications resulting from the block copolymer aspects in particular demonstrate the frontier science that resulted from this project, results that are relevant to DOE's mission in scientific discovery and innovation. Advanced lithography is critical to our nation's technological leadership and economic security.

Refereed Communications:

U. Nagpal, M. Muller, P.F. Nealey, and J.J. de Pablo, "Free Energy of Defects in Ordered Assemblies of Block Copolymer Domains," to be published in *ACS Letters*.

B.L. Peters, A. Ramírez-Hernández, D.Q. Pike, M. Müller, and J.J. de Pablo, "Non-Equilibrium Simulations of Lamellae Forming Block Copolymers under Steady Shear: A Comparison of Dissipative Particle Dynamics and Brownian Dynamics," to be published in *Macromolecules*.

Scalable Assembly of Patterned Ordered Functional Micelle Arrays 146152

Year 3 of 3

Principal Investigator: H. Fan

Project Purpose:

Successful multiscale patterning (micro- to nanometer) with precision, speed, and reproducibility at the nanoscale is crucial for rapid evolution in computer logic, memory, metamaterials, photonic crystals, plasmonics, energy harvesting and storage, and nano-bio applications. Significant advances in nanopatterning technology combine “bottom-up” directed self-assembly with “top-down” lithographies, producing sub-100 nm features. However, control of nanoscale structures in the third dimension remains an unsolved challenge. Significant technical difficulties include scalable, cost-effective, and rapid fabrication of reliable patterns with low defect densities and long-range order in various materials systems. In this project, we are studying self-assembly of amphiphilic molecular micelles to form large-area arrays on patterned surfaces, and in 3D nanoscale templates with an emphasis on compatibility with semiconductor processing for future device integration. Amphiphilic molecules form monodisperse micelles with sizes precisely defined by molecular chain length of each amphiphilic molecule, ranging from 5-50 nm. Evaporation of micellar solutions leads to highly ordered large-area micelle arrays. Dynamic micelle assembly operating under the influence of physical 1D-3D topographical templates with characteristic dimensions integer multiples of one to five times the micelle diameter will provide a means to spatially control long-range order and to direct micelle assembly into predefined hierarchical configurations. Through encapsulation, various metal, semiconductor, or magnetic nanoparticles can be introduced into the hydrophobic interior, providing unprecedented engineering of robust hybrid functional 1D-3D micelle arrays and their collective electronic, optical, or magnetic behaviors. For example, although the behavior of periodic dielectric structures, so-called “photonic crystals,” are quite well understood, the response of metallo-dielectric structures with coupled collective plasmonic and dielectric responses are quite poorly understood, despite their great potential application in advanced devices. Precise nanoscale patterning of these arrays will enable fabrication of controlled nanostructures for devices such as surface enhanced Raman sensors and photonic crystals.

Summary of Accomplishments:

Monodisperse fluorescent organic/inorganic composite nanoparticles were synthesized through spontaneous self-assembly of block copolymer polystyrene-*b*-polyvinylpyridine and rare earth ions (Europium, Terbium, Thulium, etc.). Depending on the rare earth ions selected, tunable light emission colors, including the primary red, green, and blue colors, have been accomplished. Further, by stoichiometric mixing of nanoparticles that emit different colors, the full color spectrum can be accessed. Both electron microscopy and spectroscopic characterizations confirm specific interactions of rare earth and the block copolymers. The resulting nanoparticles are monodisperse as characterized by dynamic light scattering. They are very stable and can be dispersed in common solvents and, together with homo-polymers, form ordered arrays and thin films (both supported and free standing) upon solvent evaporation. The resulting nanoparticle thin films exhibit mechanical flexibility for ease of processing or device integration.

We have demonstrated the unique assembly properties of dynamic micellar nanoparticles by combining a top down lithographic nanopatterning technique with a solution-based bottom up self-assembly. The templates for the directed self-assembly of the micelles consisted of arrays of cylindrical recess features fabricated by nanoimprint lithography. Silica was coated on this patterned substrate and subsequently selectively functionalized with a positively charged molecular monolayer

(N-(3-Trimethoxysilylpropyl) diethylenetriamine) to regulate the micelle-surface interactions. The self-assembled polystyrene-b-poly(4-vinyl pyridine) micelles were approximately 325 nm in diameter in aqueous solutions (pH = 2.5) and 50 nm in diameter in the dry state. The average number of micelles assembled per feature increased from less than 1 to 12 with increasing feature diameter in the range of 200 nm–1 μ m. Using a 2D model for maximum packing of circles in circular host features, the effective sphere size of the micelles during assembly was calculated to be 250 nm in diameter. Thus, the micelles exhibited three characteristic sizes during assembly, 325 nm in bulk solution, 250 nm during assembly, and 50 nm in the dry state.

Significance:

This work provides bottom-up methods in the synthesis and control of matter on multiple length scales. The new nanostructures and the degree of control would provide benefits to energy and national security applications. Fabrication of scalable patterned structures and facile and scalable self-assembly processes for ordered arrays, and their use as templates for metallic nanostructures in energy storage, photonic, and sensor applications, will impact DOE and DHS missions in national security.

Characterization of Failure Modes in Deep UV and Deep Green LEDs Utilizing Advanced Semiconductor Localization Techniques

147374

Year 3 of 3

Principal Investigator: M. A. Miller

Project Purpose:

Group III-nitride light emitting diodes (LEDs) are currently available with wavelengths from the deep ultraviolet (UV) to the deep green. The alloys of AlN, GaN, and InN possess tunable direct band gaps and have the potential to emit in the entire visible spectrum and well into the UV. In order to broaden the commercial availability of III-nitride LEDs, reliability, lifetimes, and low efficiencies in the deep UV and green must be improved. These parameters are tightly coupled to key materials issues including the lack of non-native substrates, alloy separation during growth, the presence of non-radiative defects within the active region, and inefficient p-type doping and hole-injection. Low growth temperatures required for higher indium compositions lead to poor crystalline quality and increased structural defect densities (V-defects) in green LEDs. Deep green and deep UV LEDs, which embody the ends of the present-day III-nitride LED spectrum and exhibit the lowest efficiencies, stand to benefit the most from reliability and failure analysis (FA) studies. Recent efforts to pinpoint a specific cause for short lifetimes and poor reliability in deep green and deep UV LEDs have utilized such methods as time-resolved photoluminescence, electroluminescence (EL), and cathodoluminescence. These characterization techniques have suggested a number of degradation mechanisms including increased nitrogen vacancies, increased nonradiative recombination sites, joule heating due to poor p-type contact resistance, current crowding, and decreased carrier injection.

This project utilizes existing nondestructive, laser-based techniques, such as thermally induced voltage alteration (TIVA) and laser-induced voltage alteration (LIVA), to determine precursors to premature degradation and failure of deep green and deep UV LEDs. Risk in this project has evolved from initial detection of electrically active defects from a high background intensity of threading dislocations to correlation of those defects initially characterized at time zero with stress-induced defects and ultimately to describe stress-induced failure mechanisms.

Summary of Accomplishments:

Through this project, we have demonstrated that laser-based techniques (LIVA and TIVA) are effective in characterizing III-nitride LEDs. The focus was on deep UV and deep green LEDs, and electrically active defect sites were localized in both. Once the defect sites were localized they were characterized with TEM cross-sections through the defective areas.

We developed a screening method that allows detection of electrically active defects in UV LEDs based on electrical characterization alone. The method can be easily performed without lengthy aging studies. Data from the electrical characterization could be used to predict the existence of defects in the UV LEDs.

Defects were observed in both the green and UV LEDs that could potentially reduce the lifetimes of the devices. In the green LEDs, dark defect signals pinpointed large contact metallization defects. Defects in the contact metallization may create strong spatial nonuniformities in current injection. This type of defect could create hotspots and nonuniform light emission. Dark defect signals observed in the UV LEDs indicated metal diffusion along dislocation cores to create leakage currents through the quantum wells. It is theorized that failure occurred in the UV LEDs when enough of these leakage paths dominated current injection through the quantum wells.

We have proven that the TIVA/LIVA characterization technique can be a successful tool for III-nitride LED localization of defects and characterization of degradation. Coupled with other electrical measurements, the TIVA/LIVA technique can be a powerful tool to predict early failure in commercial devices, as well as support the development of in-house semiconductor devices. Further studies characterizing the multiple different defects observed in the green and UV LEDs and further laser-spotting characterization are expected to fully establish the TIVA/LIVA technique as a viable screening method and reliability technique for III-nitride optoelectronics.

Significance:

We demonstrated the TIVA/LIVA characterization techniques' applicability to non-silicon technologies. We have proven that TIVA/LIVA is more sensitive to electrically active defects than other common characterization techniques (electroluminescence). We demonstrated the ability to monitor defects that changed with stress. We localized discrete undesirable processing defects at the location of the TIVA/LIVA signals. Fundamental insight into the failure modes of deep green and deep UV LEDs can be widely applied to nitride-based LEDs and laser diodes and thus to a wide range of emission wavelengths and applications, both as an in-house developmental tool and as leverage to develop industrial collaborations. Additionally, DOE's mission in energy conservation through the widespread adoption of energy-efficient solid state lighting benefits from this research.

Photoelectronic Characterization of Heterointerfaces 147942

Year 3 of 3

Principal Investigator: M. T. Brumbach

Project Purpose:

This project conducted an investigation of inorganic/organic interfaces by tailoring the surfaces for photoelectron spectroscopic characterization, in order to gain a better understanding of the role of interfacial species on the chemical and electronic properties of hybrid interfaces and to guide the improvement of device performance. We employed surface modification, patterning, and thin film deposition to critically evaluate new combinations of materials on electronic structure.

In many devices, including solar cells and transistors, the performance relies on the electronic band structure at the internal interfaces of the device. For example, the electronic offset between two materials in a photovoltaic directly relate to the output voltage of the solar cell. Poorly matched band structures may have insufficient potential offsets to drive the device, may facilitate recombination, and/or may induce barriers for charge transfer. Interfaces of organic/inorganic materials are not well understood, and research on interfacial energy alignment in these systems has been lacking. Large assumptions are prevalent, including the fact that interfacial energy level alignments are commonly assumed from bulk properties, and the effects of ubiquitous contamination are neglected. The objective of this work is to perform robust characterization of the electronic structure at real hybrid interfaces by tailoring the interfacial region for photoelectron spectroscopy. Photoelectron spectroscopy can be used to map the band structure through careful analyses of the layer-by-layer formation of an interface where ionization potential, core level positions, and work function are monitored. Interfacial self-assembled monolayers (SAM) are being utilized to induce dipoles of various magnitudes at the interface. Control of the surface work function through use of an organized mixed SAM has not been attempted, although it has been shown that mixed dipolar species do lead to a concentration-dependent ionization potential. The role of unknown species can be inferred from the energy band diagram of a real hybrid interface by understanding the role of known species in known geometries.

Summary of Accomplishments:

- Development of photoemission characterization capabilities (photoelectron spectroscopy [UPS], imaging x-ray photoelectron spectroscopy [XPS])
- Novel utilization of synchrotron-based techniques (imaging near edge x-ray absorption fine structure [NEXAFS], hard x-ray photoelectron spectroscopy [HAXPES])
- Development of deposition capabilities for organic thin films
- New understanding of polymer/inorganic interfaces
- Discovery of a new platform for evaluating charge transport in concert with XPS

Significance:

The investigations of surface patterning, use of synchrotron techniques, and study of new polymer interfaces yielded new insights on the electronic structure of hybrid interfaces and led to the discovery of a new technique for characterizing electronic and chemical properties of extremely thin films. Potential application to energy-harvesting devices such as photovoltaics positions this project to be in support of DOE/EERE's mission.

Refereed Communications:

M.T. Brumbach and J.C. Woicik, "HAXPES of Protected ITO Surfaces at the Buried P3HT/ITO Interface," *Surface and Interface Analysis*, vol. 44, pp. 1379-1384, October 2012.

Ion-Photon Quantum Interface: Entanglement Engineering

148549

Year 3 of 3

Principal Investigator: D. L. Moehring

Project Purpose:

Distributed quantum information processing requires a reliable quantum memory and a faithful carrier of quantum information. Trapped ion quantum bits (qubits) are the leading realization for quantum information storage due in large part to their very long coherence times and well developed laser interaction techniques. Photonic qubits, on the other hand, are the natural choice for the transport of quantum information as they can quickly travel long distances with a minimum of decoherence. The capability to entangle photons with trapped ions in a technologically relevant (highly efficient) and scalable fashion would be a game changing achievement. We leveraged the active and successful development of microfabricated semiconductor ion traps at Sandia's Microsystems and Engineering Sciences and Applications (MESA) facility in order to integrate micro-optical components. Compared to current efforts in academic settings combining macro-sized ion traps and optics, a micro-device will result in the dramatically increased speed and fidelity of ion-trap based quantum-networking protocols. The use of microfabricated components is also essential for the reproducibility and scalability of this technology. The combination of technical knowhow and fabrication expertise at Sandia does not exist in the academic setting. Indeed, integrating smaller components will directly allow for a stronger quantum coherent interface between a single trapped ion and a single photon. If successful, this technology could lead to new demonstrations of fundamental physics properties and would open new avenues for scalable quantum networking architectures. This effort will also result in a new quantum information science and technology (QIST) capability for Sandia and will further our strategic objectives—providing technologically relevant engineering solutions for QIST implementations.

Summary of Accomplishments:

We accomplished several important milestones in the construction, characterization, and testing of the entire ion-cavity system. The design, fabrication, and testing of a radiofrequency ion trap capable of being integrated with an optical cavity has been completed with verification of an ion being shuttled from loading hole to cavity location. Optical cavities have been designed and tested, ensuring the optical coatings are viable for performance metrics.

Full integration of the optical cavity to the ion trap has been accomplished. The designed flexure mount for holding the top mirror was characterized and resonance frequencies measured. Additionally, a process for inserting and affixing the bottom silicon mirror into the ion trap was developed and characterized. This procedure leads to a bottom mirror tilt of at most 0.1 degrees — a much higher precision than worst-case tolerance. The entire system construction has been performed with active alignment of the optical cavity to the ion trap. A full system has been constructed and inserted for testing in an ultra-high vacuum (UHV) environment. Single ytterbium ions have been successfully loaded into the trap.

Significance:

This project complements the current Intelligence Advanced Research Projects Activity (IARPA) sponsored program on quantum information. Our work pioneers an integrated approach to trapped-ion based quantum networks that provides a foundation for a scalable quantum networks and long distance quantum communication systems based upon trapped ion technologies. Additionally, it provides Sandia with a new QIST capability that can find applications in projects requiring collection of light from single atoms, and furthers the strategic objective of providing engineering solutions to QIST implementations.

Refereed Communications:

J.D. Sterk, et al., “Advanced Ion Trap Structures with Integrated Tools for Qubit Manipulation,” in *Proceedings of the APS Division of Atomic Molecular and Optical Physics Meeting*, 2012.

F. Benito, J. Sterk, B. Tabakov, R. Halti, C. Tigges, D. Stick, M. Balin, and D. Moehring, “Integrated Cavity QED in a Linear Ion Trap Chip for Enhanced Light Collection,” in *Proceedings of the APS Division of Atomic Molecular and Optical Physics Meeting*, 2012.

Polyoxometalate “Solutions” for Energy Storage 150774

Year 3 of 3

Principal Investigator: T. M. Anderson

Project Purpose:

Global energy consumption is projected to significantly increase by mid-century, and the increased need will be met, at least in part, through use of renewable energy sources. However, the intermittent nature of renewables requires advances in large-scale energy storage. Concentrating on promising flow battery technologies, we are preparing new charge storage materials with increased energy density. A primary goal of this work was to lower the cost from the current technologies. Specifically, we addressed problems associated with low solubility of vanadium(IV) and poor stability of vanadium(V) at high temperatures in the cathode of vanadium redox flow batteries. Building on the extensive inorganic synthesis and characterization expertise and capabilities at Sandia, we utilized metal-oxide clusters [polyoxometalates (POMs) for convenience] as new, dissolved charge storage materials. We applied a suite of analytical and electrochemical techniques to evaluate the stability and other fundamental properties of POMs in nonaqueous battery electrolytes in order to gain fundamental understanding of the structural and electrical properties of these unique complexes. By including non-aqueous chemistry, we had the unprecedented opportunity to work with a wider voltage window while simultaneously decreasing temperature sensitivity and increasing cycle life. In addition, prior to our work, there was a considerable paucity of data elucidating the fundamental electrochemical properties (and related protonation states) of POMs under non-aqueous conditions. The ultimate goal of the project was to incorporate POM catholytes into a redox flow cell configuration in order to store charge.

Summary of Accomplishments:

A flow battery containing POM electrolyte was constructed for the first time. A suite of POMs (from the literature as well as new compounds) were synthesized and rigorously screened for long-term stability and highly reversible electrochemical activity. The alkali and ammonium salts of POMs containing both vanadium and tungsten were identified as best candidates. Ultimately, three POMs containing both electrochemically active vanadium and tungsten were selected for testing. The aqueous Keggin ($\text{K}_6\text{HSiV}_3\text{W}_9\text{O}_{40}$) cycles a three-electron process in each static half-cell with excellent stability. To the best of our knowledge, this is the first three-electron process that has ever been observed in any flow battery chemistry. The non-aqueous Keggin ($(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}_4\text{H}_3\text{SiV}_3\text{W}_9\text{O}_{40}$) cycles a two-electron process with kinetics that are significantly more sluggish than its aqueous counterpart. An aqueous Wells-Dawson ($\text{K}_8\text{HP}_2\text{V}_3\text{W}_{15}\text{O}_{62}$) was also examined in a static cell, but it decomposes after several cycles. A flow cell was constructed using the aqueous Keggin ($\text{K}_6\text{HSiV}_3\text{W}_9\text{O}_{40}$). The flow cell has four times better charge Faradaic efficiency than the static system and two times better discharge efficiency due to the larger surface area of the membrane and the increased active surface of the electrode. In our quest to prepare optimal charge storage materials, we also prepared a manganese-containing POM single-molecule magnet that exhibits a large axial anisotropy as a result of near-parallel alignment of Jahn-Teller axes. The results were recently published in a special issue of *Dalton Transactions*.

Significance:

The impact of this work is the discovery of new energy storage materials capable of undergoing multi-electron charge/discharge processes by the variation of charge density, molecular symmetry, and metal populations. The elucidation of the properties of these metal-oxide clusters will lead to the successful preparation of additional advanced materials. This project focused on the DOE's goal to create a more flexible, reliable, and higher capacity energy infrastructure by applying advanced science and

technology to develop new materials for energy storage applications to support DOE's missions to promote carbon neutral technologies, reduce petroleum imports, and to incorporate intermittent renewable energy sources.

Refereed Communications:

X. Fang, K. McCallum, H.D. Pratt III, T.M. Anderson, K. Dennis, and M. Luban, "A Co-Crystal of Polyoxometalates Exhibiting Single-Molecule Magnet Behavior: The Structural Origin of a Large Magnetic Anisotropy," *Dalton Transactions*, vol. 41, pp. 9867-9870, March 2012.

Elucidating the Role of Interfacial Materials Properties in Microfluidic Packages 150968

Year 3 of 3

Principal Investigator: T. L. Edwards

Project Purpose:

Microsensors for chemical and biological detection have seen relatively little field application because the small size and low cost of the microsensor are offset by the large size, high cost, and complexity of the balance of the sensing system — principally, the required external pumps and valves. Attempts have been made to integrate these components into the sensor's microfluidic package but success has been limited by the lack of software design tools to simulate microfluidic device performance. Software simulation, in turn, is limited by our understanding of the materials properties at the interfaces of plastic laminate layers comprising the package. This project will address these shortcomings by designing experiments to extract the relevant mechanical, thermal, electrical, and chemical properties of plastic laminate interfaces; developing a multiphysics model incorporating these parameters for plastic laminate microfluidic devices; demonstrating the model's capabilities by designing, fabricating, and testing a microfluidic pump.

A number of technologies have been employed to create microfluidic packages for microsensors, including silicon and glass micromachining, ceramic laminates, plastic injection molding, hot embossing, cast molding, and plastic laminates. Of these, plastic laminate packaging provides an attractive combination of low capital and material cost, rapid prototyping, and complex mechanical and fluidic structures. This technology employs a variety of thin polymer and metal films bonded by adhesives, solvents, thermal fusion, and ultrasonic welding. The properties of these interfaces—thermal and electrical conductivity, mechanical deformation, adhesion strength, and chemical resistance—vary from the bulk properties of the laminate films and depend on the laminate composition and joining method employed. These interface properties are the focus of this project. We will develop the experimental techniques required to measure them, use this information to populate a multiphysics model describing plastic laminate behavior, and as a proof of concept demonstration, apply this model to design an integrated micropump, a critical component for high-performance microfluidic systems.

Summary of Accomplishments:

We implemented a multiscale, heterogeneous, cohesive model in a COMSOL finite element program. This is unique and important because it allows integration of the model with other physical packages, extending the capability toward more accurate isolation of unique contributions from various internal variables of interest associated with the cohesive layer and how they interact with the adherends. In this model, we also included a fracture or damage component.

We created a simple-to-fabricate test structure that utilizes the constrained or unconstrained blister test. This test is important for determining the energy expended in delamination of a thin layer joined to a thick adherend. The structure is particularly useful for our work in pseudo 3D micro- and mesoscale fluidic structures in which pressurized channels, valves, pumps, and integrated components are often utilized. The constrained blister test is useful for relating the released energy of delamination (isolated from other processes such as plasticity and elasticity) and can be related to the multiscale cohesive model described earlier. Thus, these two methods allow for extraction of the internal variables of the custom interface.

We created joining methods for thin plastic laminates of various materials (polyethylene, polymethylmethacrylate, polyetherurethane, polyethyleneterephthalate, and glass) of various thicknesses

(ranging from 0.0005” to 0.125”). These methods include adhesive joining using acrylic and silicone-based adhesives, solvent welding, thermal welding, and laser welding. The adhesive and laser welding were of interest because of the ability to control the weld pattern and create interesting structures.

Significance:

This research has already significantly impacted design and fabrication of sensor platforms in several projects. One project will result in an invention disclosure from the design of a simple and inexpensive, yet effective valve in a simple package. The result of this package and valve design was the acceleration of field-testing for the sensor. Potential impact is in the extension of this continuum mechanical model on elucidating interfacial properties in other difficult to understand interfaces. Applications to chemical and biological sensors using microfluidic technologies are of interest to several agencies including DHS and DTRA.

Refereed Communications:

P.R. Miller, S.A. Skoog, T.L. Edwards, D.R. Wheeler, X. Xiao, S.M. Brozik, R. Polsky, and R.J. Narayan, “Hollow Microneedle-Based Sensor for Multiplexed Transdermal Electrochemical Sensing,” *Journal of Visualized Experiments*, vol. 64, e4067, DOI: 10.3791/4067, June 2012.

J.C. Harper, T.L. Edwards, T. Savage, S. Harbaugh, N. Kelley-Loughnane, M.O. Stone, C.J. Brinker, and S.M. Brozik, “Biosensing: Orthogonal Cell-Based Biosensing: Fluorescent, Electrochemical, and Colorimetric Detection with Silica-Immobilized Cellular Communities Integrated with an ITO–Glass/Plastic Laminate Cartridge,” *Small*, vol. 8, p. 2613, September 2012.

T.L. Edwards, J.C. Harper, R. Polsky, D.M. Lopez, D.R. Wheeler, A.C. Allen, and S.M. Brozik, “A Parallel Microfluidic Channel Fixture Fabricated using Laser Ablated Plastic Laminates for Electrochemical and Chemiluminescent Biodetection of DNA,” *Biomicrofluidics*, vol. 5, p. 044115, December 2011.

Nanoscale Mechanisms in Advanced Aging of Materials During Storage of Spent “High Burnup” Nuclear Fuel

151328

Year 2 of 3

Principal Investigator: B. Clark

Project Purpose:

The decision not to pursue Yucca Mountain as a nuclear waste repository implies that spent nuclear fuel will have to be stored in a retrievable condition (with claddings maintaining necessary strength and ductility) for an indeterminate amount of time, conceivably on the order of centuries. Compounding this issue is the trend to discharge nuclear fuel after “high burnup,” (i.e., > 45 GWd/MTU). Although the US has 25 years experience in storage of low burnup fuel, there is no precedent for storage of high burnup fuel, where increased radiation dose, hydrogen uptake, and corrosive processes can significantly influence the mechanical properties of the cladding.

The purpose of this project is to understand the degradation mechanisms in claddings during high burnup and in dry storage. This is needed to develop extrapolative, physics-based models that can predict mechanical integrity of the cladding in order to provide fidelity in the ability to retrieve used fuel from storage either for transportation or further processing. The details of these nanoscale degradation mechanisms are being pursued using in situ gas-phase transmission electron microscope (TEM) experiments and by ex situ hydriding and ion irradiation experiments.

With a state-of-the-art gas cell TEM stage, advanced electrochemistry lab, and the new Ion Beam Lab, Sandia is poised to explore experimental realms previously unattainable. Fundamental understanding regarding evolution of corrosive mechanisms, defect structures, and formation/reorientation of hydrides as a function of burnup and/or storage conditions, all critical for predicting long-term cladding integrity, will be obtained by combining these world-class facilities with expertise in irradiation defects, electrochemical material properties, and microstructural characterization and evolution.

Active Infrared Plasmonics

151329

Year 2 of 3

Principal Investigator: E. A. Shaner

Project Purpose:

The mid-infrared ([mid-IR], 3–12 microns) is a highly desirable spectral range for imaging, environmental sensing, and countermeasures. We propose to develop a new class of mid-IR devices, based on plasmonic and metamaterial concepts, which are dynamically controlled by tunable semiconductor plasma resonances. It is well known that any material resonance (phonons, excitons, electron plasma) impacts dielectric properties; our primary challenge is to implement the tuning of a semiconductor plasma resonance with a voltage bias. We have demonstrated passive tuning of both plasmonic and metamaterial structures in the mid-IR using semiconductor plasmas. In the mid-IR, semiconductor carrier densities on the order of $5 \times 10^{17} \text{ cm}^{-3}$ to $2 \times 10^{18} \text{ cm}^{-3}$ are desirable for tuning effects. Gate control of carrier densities at the high end of this range is at or near the limit of what has been demonstrated in literature for transistor-style devices. Combined with the fact that we are exploiting the optical properties of the device layers, rather than electrical, we are entering into interesting territory that has not been significantly explored to date.

The primary reason for this work is that external interests have identified the voltage control of resonances as being high risk. Even though we have demonstrated passive mid-IR control of both plasmonic and metamaterial structures using semiconductor plasmas (by varying the density in doped epi-layers of GaAs and InSb), they are correct in identifying the dynamic tuning as the key effect needed for this research to progress. Once that capability has been demonstrated, electromagnetic simulations of plasmonic- and metamaterial-based beam-steering elements, reflectance modulators, filters, and emission control structures should reliably guide development efforts based on the known behavior of semiconductor device layers. While all of these potential applications have mechanical alternatives, it is well known that achieving similar functionality in nonmechanical solutions is desirable in terms of reduced size, weight, power requirements, and response times.

Monolithically Integrated Coherent Mid-Infrared Receiver

151332

Year 2 of 3

Principal Investigator: M. Wanke

Project Purpose:

In this collaboration between Sandia and a multi-university National Science Foundation Engineering Research Center (NSF-ERC) project at Princeton University, we are working toward the development of a coherent mid-infrared (MIR) receiver with the goal of achieving mid-infrared detectivity 100 times better than state-of-the-art room temperature MIR photodetectors. Conventional MIR photodetectors suffer from excess dark current due to thermal excitation of carriers at room temperature. Our goal is to use the nonlinear electrical response of a Schottky diode detector instead of the linear optical absorption response in photodetectors, and therefore eliminate dark current issues. Schottky detectors are commonly used at lower frequencies where they are integrated with antennas to couple light to the small diode. Although extremely sensitive at low frequencies, their sensitivity at higher frequencies has been limited due to the device capacitance, which shunts higher frequency signals from the antenna around the diode. We recently demonstrated an antenna-less method of coupling THz radiation to a Schottky diode, by inserting a diode active region directly into a laser core and using the surface plasmon to couple radiation into the diode. In this project, we are exploring whether this new coupling geometry reduces the capacitive shunting and can enable highly sensitive integrated coherent mid-infrared detectors.

There are many uncertainties in this work: Does the new geometry eliminate the capacitance issue? Will the required surface plasmon coupling significantly impact the laser performance? Can planar Schottky diodes operate above a few THz? Can the mixer RF response be coupled out with this geometry? While a Schottky diode heterodyne mixer could have significant application impact, this initial demonstration is focused on understanding these basic questions.

Non-Abelian Fractional Quantum Hall Effect for Fault-Resistant Topological Quantum Computation

151333

Year 2 of 3

Principal Investigator: W. Pan

Project Purpose:

The purpose of this project is to understand non-Abelian quantum Hall physics in order to obtain a scientific foundation for topological quantum computation (TQC) applications. We are attempting to fabricate interferometer devices and carry out quantum interference measurements in these devices. Success of this project will allow us to gain a deeper understanding of non-Abelian physics and is expected to have a great impact on the feasibility of eventually building a topological computer.

Modern encryption method is based on the assumption that it is impossible to prime-factorize a large digit number within a reasonable time frame. Indeed, it is estimated that factorizing a 200-digit number would require 170 CPU years using an Intel computer. This estimate, however, is drastically changed with the use of a quantum computer, which has been theorized to be capable of readily factorizing a 300-digit number. After more than 15 years of research on quantum computation, many fundamental issues remain unresolved. For example, the strong coupling between electrons and their local environments greatly reduces electron coherence time and requires complex error-correction schemes to manipulate quantum information before it is lost. As such, there is a pressing need to identify new paradigms, which can potentially enable revolutionary advances in the field of quantum computation.

TQC has emerged as one of the most promising approaches. Under this approach, the topological properties of a non-Abelian quantum system, which are insensitive to local perturbations, are utilized to process and transport quantum information. The encoded information can be protected and rendered immune from nearly all environmental decoherence processes without additional error-correction. It is generally believed that the low energy excitations of the so-called $\nu=5/2$ fractional quantum Hall state may obey non-Abelian statistics. Our goal is to explore this novel fractional quantum Hall (FQH) state and to understand and create a scientific foundation for exploiting this quantum matter state in order to build a knowledge base for the emerging TQC technology.

Germanium on Silicon Optoelectronics 151334

Year 2 of 3

Principal Investigator: P. Davids

Project Purpose:

Moore's law scaling of microprocessor technology dictates that, within 10 years, power consumption in large-scale computers will be dominated by their electrical interconnects. One technology that has emerged as a potential solution to this bottleneck is silicon photonics. Yet, any optical interconnect is incomplete without a light source; owing to its indirect bandgap, creating a homogeneously integrated optical source on a silicon platform has been the single most scientifically challenging problem in the field since its inception more than two decades ago. While heterogeneous wafer bonding of III-V laser sources to silicon photonic circuits has been demonstrated, this solution is ultimately undesirable due to both incompatibility with state of the art silicon fabs and yield issues. Recently, an optically pumped strained germanium on silicon laser was reported. This preliminary result indicates that, with rigorous scientific analysis, an efficient electrically pumped laser source emitting in the technologically relevant communications wavelength band may be possible. Germanium does not suffer from the same incompatibility with complementary-metal-oxide-semiconductor (CMOS) processes as III-V heterogeneous integration technologies. Further, germanium offers the ability to directly integrate a germanium receiver on a silicon platform, which enables direct integration with CMOS electronics reducing electrical parasitics and enabling high speed, low noise, and low power receivers. The combination of these two scientific achievements would enable complete low power photonic networks homogeneously integrated in silicon.

Development of an electrically pumped laser emitting at relevant optical communications wavelengths in a group IV semiconductor has never previously been achieved. Only through rigorous analysis of the band-structure, strain, doping concentration, and growth conditions will a successful demonstration be possible. Demonstration of an electrically pumped germanium-on-silicon laser would be the most significant scientific and technological breakthrough in the field of silicon photonics since its foundation, an enabling accomplishment for the future of the silicon photonics platform.

We have fabricated sample structures and are completing an experimental matrix study of the optical properties of Ge under different growth methods and different doping techniques. Analytic characterization of these results will be performed for accurate determination of active doping profiles and strain and the results will be correlated with measured sample photoluminescence. We will completely characterize our newly developed waveguide gain structures under optical and electrical injection conditions. The measured gain and absorption will be compared to the model gain calculation and the impact of strain and doping quantified. We will perform device simulations on a novel high-gain bandwidth avalanche photodiodes. We will design, fabricate, and test Ge avalanche photodiodes in our Si photonics platform and attempt to demonstrate a gain bandwidth product exceeding 340 GHz. We will also examine high-power linear Ge photodiodes for RF applications.

Fundamental Investigation of Chip-Scale Vacuum Micropumping (CSVMP) 151335

Year 2 of 3

Principal Investigator: R. P. Manginell

Project Purpose:

If ever-important microtechnology like micro-mass-spectrometers or miniature atomic clocks are to be fielded, a Chip-Scale Vacuum Micropump (CSVMP) must be developed. Neither device can function for long in the field without a CSVMP. Yet, despite ~20 years of Defense Advanced Research Projects Agency (DARPA) funding, a truly useful CSVMP remains unrealized. The best designs generate 21 kPa (3 PSI) below atmospheric pressure and 5 cm³/min flow. Are technological barriers to blame, or more fundamental issues? This project is taking a focused approach to answering this question.

Creating a vacuum micropump is undoubtedly challenging given the lack of lubricated seals on this scale and low relative dimensional/assembly tolerances. Importantly, the micropump literature does not consider the magnitude of leaks from free molecular flow (FMF) to continuum flow. The magnitude of FMF and transition flow leaks in nanoscale roughness is something for which very few measurements have been made, and theoretical understanding is lacking.

The foundational question posed herein is novel: Is a gas micropump an impossibility or just a technical headache? Direct sponsors are interested in the technology, not the fundamentals.

This project will, for the first time, create an experimental platform for measuring micropump leaks at rates three orders of magnitude lower than previous literature work. Modeling/simulation is being performed and compared with the results of these experiments, providing the first micropump-relevant validated models. Theoretical understanding of transition and slip flows on these scales is nascent and this project will contribute significantly to the field. The best method of modeling/simulation from transition to FMF is Direct Simulation Monte Carlo (DSMC), which requires massively parallel processing such as that available at Sandia. Validated models will be used to draw conclusions regarding fundamental CSVMP operation and to determine parameters for a functioning CSVMP.

Coherent Phonon Generation through Nanoscale Enhanced Light-Matter Interaction: Towards Novel Silicon Lasers, Broadband Phononic Signal Processing and Optically Powered Micromechanics
151336

Year 2 of 3

Principal Investigator: P. T. Rakich

Project Purpose:

The science of nanoscale light-matter interactions, specifically the study of optical forces and photon-phonon coupling within nanoscale materials and geometries, provide fertile ground for tremendous scientific and technological advancement. Through deeper understanding of the physics of coherent phonon generation, new ultrafast methods for the study of thermal transport, phonon lifetimes and phonon dispersion within novel materials and nanoscale structures will be possible. Furthermore, improved understanding of optical force mediated photon-phonon coupling will enable efficient light-driven coherent phonon generation; such processes can be utilized to create significant improvements in radio frequency (RF), phononic, acousto-optic and optical signal processing performance via a new class of chip-scale hybrid photonic-phononic devices. However, these scientific and technological advances will require a new experimental and theoretical foundation for the study of light-matter interactions. Through this project, we propose develop this scientific foundation by: 1) developing powerful new multiscale models for the treatment of optical force mediated photon-phonon coupling at all length scales, 2) developing rigorous models for the prediction of optical forces within nanoscale materials and geometries, and 3) devising a flexible experimental platform for the study of optical forces and photon-phonon coupling at nanoscales. In achieving the aforementioned theoretical and experimental tasks, we will radically advance the science of nanoscale light-matter interactions. In the process, Sandia's unique Microsystems and Engineering Sciences and Application (MESA) capabilities will be used to execute highly differentiated scientific studies and to develop highly differentiated chip-scale technologies of tremendous benefit to DOE's mission.

Photodefined Micro/Nanostructures for Sensing Applications 151337

Year 2 of 3

Principal Investigator: R. Polsky

Project Purpose:

The advancement of materials technology towards the development of ultrasensitive sensors for the detection of biological and chemical agents has been a longstanding challenge. The purpose of this project is to explore various lithographic techniques to make structures in photopatternable materials and explore chemical and material modifications to design novel sensing platforms. The key attributes that we intend to explore are as follows: 1) Pattern structures for sensing applications using interference lithography and direct laser writing techniques such as two-photon fabrication and stereolithography, 2) explore patterning in photosensitive materials such as photoresist, and 3) explore methods to improve the interfacial chemistry of the electrode surface to immobilize recognition elements, signaling pathways, anti-fouling components, etc., including nanoparticle and conducting polymer modifications. The resulting electrode can be tailored for specific applications and integrated into sensing platforms for the detection of chemical and biological threats.

Theoretical and Experimental Studies of Electrified Interfaces Relevant to Energy Storage

151338

Year 2 of 3

Principal Investigator: C. C. Hayden

Project Purpose:

Major advances in electrochemical technologies for energy storage require improved understanding of electrolyte/electrode interfaces, including structure, interfacial species, and electrochemical processes, and the incorporation of this understanding into quantitative models. Such models will guide development of advanced designs and materials to increase efficiency and reduce aging and failure rates. Simplified models such as Helmholtz's electric double-layer (EDL) concept and even Gouy-Chapman-Stern's diffuse model fail to take into account the molecular nature of ion distributions, solvents, and electrode surfaces; therefore, it cannot be used in predictive, high-fidelity simulations for device design. The goal of this project is to develop detailed models of the structure and chemical properties of representative electrified interfaces, which we will validate by multiparameter, minimally invasive experimental measurements. Emerging laser technology only now becoming possible with Sandia's rapid development of atomistic-to-continuum interfacial modeling and recent advances in spatially precise in situ optical probes enables such synergistic interaction between calculations and experiment. Much of previous work in this field has focused on complex, integrated electrochemical energy-storage devices and/or materials that are not suitable for detailed modeling and in situ probing. Our approach attempts to gain a predictive understanding of complex interfaces present in such devices through coordinated experimental and theoretical studies of tractable (model) systems, which isolate important phenomena. Experimentally, we will employ second harmonic generation (SHG) microscopy and Stark shift spectroscopy to measure spatially resolved interfacial electric fields. A combination of Raman microscopy, polarization modulation reflection absorption infrared spectroscopy (PM-RAIRS) and surface sum frequency generation (SFG) will identify species. While the project is both computationally demanding and experimentally challenging, we have previously demonstrated successes in the related computational areas and in laser-based confocal microscopy and combustion diagnostics. Furthermore, we will leverage recent investments made by Sandia in massively parallel computing and will take advantage of emerging ultrafast laser technology for improved sensitivity in nonlinear spectroscopy.

Developing Thermoelectric Cryo-Cooling 151339

Year 2 of 3

Principal Investigator: D. L. Medlin

Project Purpose:

Many Sandia systems require low-temperature cooling near 77 K, including space-based-electronics for remote-sensing/verification programs, and terrestrial devices such as photon detectors, mirrors, integrated circuits, and chem-bio sensors. However, conventional cryogenic coolers are large, expensive, high-powered, and difficult to integrate with electronics. On-chip, solid-state thermoelectric (TE) cryo-cooling can reduce cost and inefficiencies, enabling future systems.

TE performance requires a high figure-of-merit, zT , optimized by high electrical conductivity, high thermopower, and low thermal conductivity — properties found in Bi-based alloys. However, commercial state-of-the-art materials are limited to $zT \sim 1$, too low for real cooling applications that must constantly remove heat from a power source. Recent reports of nanostructured bulk materials have shown $zT \sim 1.6$, largely through reduced thermal conductivity. Further advances demand corresponding improvements in electric conductivity and thermopower.

Theory predicts 10-fold zT improvements in one-dimensional nanowires (diameters < 5 nm) due to quantum confinement, which creates peaks in the electronic density-of-states that enhance thermopower. Nevertheless, the present performance of nanowires is abysmal: the best reported $zT = 0.12$. A detailed literature review suggests that this failure is due to inadequate attention to key materials factors (composition and crystallinity) affecting the electronic transport.

Our goal is to enhance thermoelectric performance at cryogenic temperatures using nanowires optimized for structure, composition, and dimensionality through an integrated program of synthesis, characterization, and theory. We will use novel electrochemical deposition approaches to provide the necessary materials control, we will employ advanced microscopies (atomic resolution transmission electron microscopy and atom probe tomography) to thoroughly evaluate material composition and structure, and we will measure the resulting transport properties on individual nanowires using novel probe platforms, guided by past theory and new modeling of nanoscale transport processes. Finally, we will fabricate and test cooling modules from TE nanowire arrays to establish the practical feasibility of this approach for cryogenic cooling.

Improving the Electrical and Thermal Resistance of Nanoscale Contacts 151340

Year 2 of 3

Principal Investigator: R. E. Jones

Project Purpose:

A fundamental factor limiting the performance of electronic and optoelectronic devices is the thermal and electrical resistance of the ubiquitous metal-semiconductor contact. This problem becomes more acute at the nanoscale where these interfacial resistances can dominate and are typically a source of failure either during fabrication or in service. While these effects have been studied extensively and are relatively well understood in bulk contacts, much of the physics must be re-evaluated for metal-nanostructure contacts due to the low dimensionality affecting central parameters such as electrostatic interactions, strain, and interfacial energies. Pragmatically, this reconsideration is warranted as bulk techniques for improving contact properties have been shown to be ineffective or inappropriate for contacts to low dimensional structures. Moreover, the techniques that do work (e.g., high-temperature annealing) are not always reliable or completely understood, leading to a cookbook approach to fabrication.

In response, our research effort is to discover the limiting factors governing electron and phonon transport at contacts to nanotubes and nanowires. The combined experimental, simulation, and theory thrusts are establishing the fundamental physics of nanoscale contacts that will enable the realization of controllable contacts to nanostructures.

We have, thus far, discovered a number of technologically useful principles. Through simulation, we can show that the ability of annealing to remove a Schottky barrier can be explained by structural changes at the contact. Also relevant to the electrical aspects of contacts, we have shown in quasi-1D devices that the gate electrode can modulate the contacts to produce sharp and stable switching characteristics needed by useful transistor devices. With regard to the thermal aspects of contacts, we now understand the bonding and structural parameters where the Kapitza resistance is dominated by a phonon bridge versus coherent interface effects.

Advanced High-Z NanoScintillators 151341

Year 2 of 3

Principal Investigator: B. A. Hernandez-Sanchez

Project Purpose:

Scintillators detect radiation by producing light upon exposure; unfortunately, the current detection quality suffers from performance and reliability issues (i.e., low luminosity, volume restrictions, chemical instability). Critical to overcoming these constraints are the elucidation of radiation interaction mechanisms for scintillating materials at multiple length scales (nano-micro-meso) and the discovery of novel high-Z nanoscintillators for γ -ray detection. The goal of this project is to determine the utility of size-selected high Z transition metal chalcogenides (MEx, E = S, Se, Te) as novel scintillating materials. Without these improved scintillator materials, the correct identification/detection of radiation sources continues to be a vulnerability to America. For the scintillation community to fully embrace nanomaterials and ultimately attract outside customers (DOE, DHS, Defense Threat Reduction Agency), it is critical that fundamental materials research be undertaken addressing the optimal crystallite size (nano-meso) and the development of new materials.

The development of novel scintillation materials and nanoscintillators is neither widespread nor established. Several key aspects prevent pursuit of these materials by industrial and academic researchers: 1) single crystal growth techniques must be used to validate a materials performance for gamma-ray spectrometers, which restricts the range of materials examined; 2) understanding of theoretical/fundamental radiation-detection physics occurring in materials is still under debate, and this precludes research into nanomaterials; and most important, 3) many researchers have limited access to radiation characterization facilities. With its multidisciplinary interactive researchers, Sandia is ideally suited to improve scintillators, using expertise and capabilities already in place to address critical materials, characterization, and production of scintillator devices.

Existing scintillator issues will be overcome as follows: 1) we are systematically evaluating oxide scintillator size effects (nano-meso); 2) we are developing novel size-controlled scintillators based on unexplored high-Z transition metal chalcogenides (MEx); 3) we are exploring the effect of activator concentration on properties; and 4) we are developing nanocomposite materials for device development. The expected results promise to revolutionize current scintillator detector capabilities.

Tailoring Thermal and Electric Transport Properties through Solid State Self-Assembly

151343

Year 2 of 3

Principal Investigator: J. Ihlefeld

Project Purpose:

To be viable as devices for high-impact energy scavenging, thermoelectric devices must be composed of nontoxic and abundant elements and be stable in air to high temperatures. Currently the best moderate temperature range (0 to ~800 °C) thermoelectrics are semiconductors comprised of relatively toxic and strategically limited p-block elements (i.e., tellurides, antimonides, and selenides). Many oxide materials would meet requirements for large-scale impact; however, their thermoelectric figures of merit ($ZT = TS^2s/k$, where T is the temperature, S is the thermopower, s is the conductivity, and k is the thermal conductivity) must be improved. The challenges for oxide thermoelectrics are low electronic conductivity and high thermal conductivities. While p-type oxides with ZT values approaching 0.8 have been identified, complementary n-type materials with equivalent ZTs have not been prepared. Virtually all groups researching oxide thermoelectrics focus on single-phase homogeneous ceramics, thin films, and single crystals.

There have been recent reports of improved thermopower in highly reduced oxide ceramics with increased carrier concentrations and phonon scattering in defective regions and separate reports of decreased thermal conductivity in oxide films with complex layered atomic arrangements. In this project, we are combining the benefits of these two studies through two approaches: 1) developing oxide ceramics with self-assembled nanostructured phases in the systems SrNbO_3 and $\text{Zn}(\text{Ga},\text{Mn})\text{O}_4$ where amphoteric dopants and processing atmospheres can be used to arbitrarily control carrier concentrations, while thermal treatments can control boundary geometries concentrations, and 2) designing oxide materials where the mechanisms controlling electronic and thermal conductivity occur on separate crystal sublattices—a so-called phonon-glass electron-crystal in a perovskite crystal structure. These methodologies have yet to be investigated by other researchers for thermoelectric applications in oxide materials—those that are environmentally benign and abundant.

Understanding and Controlling Low-Temperature Aging of Nanocrystalline Materials

151344

Year 2 of 3

Principal Investigator: C. C. Battaile

Project Purpose:

Nanocrystalline metals offer exceptional properties (e.g., high strength, fatigue resistance, radiation hardness, and low friction). The greatest hurdle to applying these materials is the fact that their grain structures evolve at ambient temperatures, and recent evidence indicates that nanocrystalline metals can even evolve at cryogenic temperatures faster than they do at room temperature. This can degrade properties and even accelerate failure. For example, large grains initiate fracture during fatigue of nanocrystalline nickel coatings, and coarsening of nanocrystalline copper lines in integrated circuits degrades their electronic properties. Still, low-temperature grain growth remains a mystery. Microstructures are usually thought to be stable below about 40% of the melting temperature. This is because the grain boundary velocity, v , is the product of the driving pressure, p , and the boundary mobility, M , which decreases exponentially with temperature. Using parameters measured in aluminum, for example, the velocity of nanoscale grain boundaries is about 40 micrometers per second at 70% of the melting temperature, but only about 1 femtometer per second at room temperature. According to these data, then, at cryogenic temperatures the boundaries should not move perceptibly within the lifetime of the universe! So how can we explain, and ultimately control, ambient-temperature grain growth in nanocrystalline metals, so that we might develop strategies for mitigating the inherent instability of these otherwise advantageous materials?

We are using a combination of experiments and simulations to unravel the mysteries of low-temperature nanostructure evolution in nanocrystalline metals. We will continue our suite of indentation experiments in both ambient and cryogenic environments to isolate the variables responsible for enabling low-temperature growth, and to ascertain the conditions, material characteristics, and ultimately, the mechanisms underlying this phenomenon. To this end, we are pursuing several techniques, including high-throughput molecular dynamics, in situ nanoindentation in the focused ion beam scanning electron microscope, precession transmission electron microscope imaging, and cryoindentation in the synchrotron, for characterizing the types of grains and interfaces that are prone to low-temperature migration.

Fundamental Investigation of CVD Graphene Synthesis 151377

Year 2 of 3

Principal Investigator: M. T. Brumbach

Project Purpose:

Graphene, a single atomic layer of sp^2 -bonded carbon, has been of significant interest to basic sciences and engineering and research in this area was awarded the 2011 Nobel Prize in physics. Among its unique properties are exceptional mechanical strength, from the strong carbon-carbon bond, high in-plane thermal conductivity, high carrier mobilities, since electrons travel through graphene as mass-less Dirac fermions, and quantum effects (such as the quantum Hall effect), which can be observed at room temperature. High-quality, large-area graphene has the potential for many exciting applications. While much larger than mechanically exfoliated graphene, chemical vapor deposition (CVD) synthesized graphene does not exhibit the same quality of physical properties. However, the potential for scalability of graphene CVD processing is extremely attractive, and this is the most promising method for its commercial viability. Through this investigation of the fundamental science behind CVD graphene growth, graphene with physical properties similar to that of mechanically exfoliated graphene will be realized on a large and inexpensive scale.

The first CVD grown graphene on copper was shown to be polycrystalline, with domain sizes of a few micrometers and exhibited lower electrical and thermal conductivities than the mechanically exfoliated graphene. The domain boundaries are likely to be a limiting factor in the CVD grown graphene and synthesis strategies need to be improved to produce near defect-free graphene. The ability to produce graphene in large areas with a commercially viable CVD technique is extremely attractive and the intent of this work is to examine deposition conditions, substrate surface effects, and the mechanisms leading to nucleation and growth of graphene. From these fundamental insights, strategies can be developed to deposit large area, high-quality graphene with significantly improved performance characteristics. This project, a collaboration with UT-Austin, has already produced CVD single crystal graphene domains over 0.5 mm across.

Epsilon-Near-Zero Material for Electromagnetic Energy Transport through Subwavelength Channels

152504

Year 2 of 2

Principal Investigator: G. S. Subramania

Project Purpose:

Efficient transport of electromagnetic energy through subwavelength channels in the optical regime can dramatically enhance the performance of subwavelength imaging, photovoltaics, sensing and light emission. Current approaches based on plasmonic structures or negative index metamaterials tend to be lossy due to material absorption and have a small bandwidth due to reliance on resonance behavior. We are using epsilon-near-zero (ENZ) material to achieve efficient subwavelength electromagnetic energy transport. ENZ materials have near-zero dielectric constant (epsilon) in the effective medium limit resulting in an unusually large effective wavelength even at optical frequencies, thus enabling energy squeezing and transfer through subwavelength channels with lower losses over larger bandwidth. ENZ material has been investigated theoretically and experimentally in the microwave regime but remains a challenge in the optical regime due to difficult nanofabrication requirements. Experimental realization in the optical would enable a whole new generation of nanophotonic systems. We are pursuing an approach of combining materials with negative (e.g., metal) and positive (e.g., SiO₂) dielectric constants to obtain materials with an effective bulk ENZ. We are exploring theoretically and experimentally in one dimension the potential and limitations of this approach in subwavelength energy transfer and emission modification of nanoscale emitters. Basic understanding obtained in the one-dimensional system will be critical for implementation in higher dimensions.

ENZ materials provide a powerful, innovative route to achieve broadband, subwavelength energy transport with low loss by exploiting the previously untapped vanishing dielectric constant regime. Current experimental work is mainly in the microwave regime. Since metal dielectric properties are considerably different at microwave frequencies, experimental demonstration at optical frequencies is a significant step both from a scientific and practical standpoint and not a mere extension. Many important applications enhanced by ENZ (mentioned earlier) are at the optical regime especially the possibility of ultrasmall optical nanocircuitry to one day surpass Moore's law limitations.

Summary of Accomplishments:

We have designed a one-dimensional implementation of ENZ structure based on a metal-dielectric multilayer stack to have an ENZ response at visible wavelengths (~ 660 nm). We selected Ag for metal due to its high plasma frequency and low loss. Through finite difference time domain simulations, we discovered for the dielectric component TiO₂ was most suitable compared to other possibilities as it better approximated an effective medium when layered with Ag. We fabricated 4-, 5- and 9-pair structures from Ag and TiO₂ of thicknesses 16 nm and 54 nm, respectively. Through spectroscopy, we observed transmission response consistent with ENZ behavior at visible wavelengths with some expected discrepancies attributable to deviation of layer thicknesses and material properties from the ideal. We also found that the metal absorption effects were still significant despite its small fraction (23% of Ag) in the ENZ system. We explored a grating structure made from the ENZ composite, which simulations indicated would improve transmission at the ENZ wavelength. We created the grating structure using focused ion beam milling and measured the optical spectrum to verify the predictions of the simulations. We observed a few percent improvements in ENZ transmission but scattering effect due surface roughening on milling reduced this effect. We plan to submit the results for publication. Since an important goal of this project is light transport through subwavelength channels, we have explored theoretically, a structure consisting of periodic array of subwavelength double groves etched

into a thin Au film. We have demonstrated that this structure enables EM energy to be squeezed to an area $(\text{wavelength}/500)^2$ across a broad wavelength range. A nonresonant mechanism wherein the charges in the metal respond instantaneously to the incoming EM field is responsible for this behavior.

Significance:

Control and efficient electromagnetic energy transport through subwavelength channels at optical frequencies is a key scientific challenge that affects many areas of photonics closely linked to DOE's mission of energy independence (e.g., photovoltaics, optical nanocircuits and efficient lighting) and national security (e.g., sensing, imaging). To this end, we have demonstrated that an ENZ composite structure can be fabricated to operate at visible frequencies using an Ag/TiO₂ multilayer composite. This can open up new frontiers in the areas mentioned above. A key issue to address is compensation of metal-induced losses that will enable these structures to be viable practical devices.

Refereed Communications:

G. Subramani, S. Foteinopoulou, and I. Brener, "Nonresonant Broadband Funneling of Light via Ultrasubwavelength Channels," *Physical Review Letters*, vol.107, p. 163902, October 2011.

High-Mobility 2D Hole Systems for Quantum Computing Applications

152505

Year 2 of 2

Principal Investigator: L. A. Tracy

Project Purpose:

One of the leading candidates for a solid state quantum bit is the spin of a single electron confined in a semiconductor. Coherent control of individual electron spins has already been demonstrated in quantum dots. These groundbreaking experiments utilized high-mobility 2D electron systems in GaAs/AlGaAs heterostructures grown via molecular beam epitaxy (MBE). The major source of decoherence in such experiments is coupling between electron spins and nuclear spins in the host GaAs semiconductor. It has been proposed that hole spins in GaAs would be better suited for such experiments due to a lesser coupling between hole and nuclear spins. Recent experiments have already shown that the dephasing time for hole spins in GaAs quantum dots is at least one order of magnitude longer than that of the electron spin.

Building on recent successes in the growth of high-mobility 2D hole systems (2DHS) via carbon doping of (100) oriented GaAs/AlGaAs heterostructures, we propose to develop 2DHS at Sandia to enable experiments investigating the physics of hole spins in GaAs, looking toward eventual applications in the area of quantum computing. This work will leverage Sandia's unique, world-class capabilities in MBE growth of GaAs/AlGaAs heterostructures and expertise in low-temperature measurements.

Summary of Accomplishments:

We demonstrated a 2DHS with mobility $\sim 5 \times 10^5 \text{ cm}^2/\text{Vs}$ at a density of $6.5 \times 10^{10} \text{ cm}^{-2}$ and temperature of 0.35 K. This mobility corresponds to a mean free path of about $\sim 1 \text{ }\mu\text{m}$, which should be long enough to allow for the fabrication of nanostructures (e.g., quantum dots) that are not dominated by impurities or defects. Magnetotransport showing the quantum Hall effect confirmed that the heterostructure contained a single 2D hole layer. We were also able to tune the hole density over a wide range by use of a Schottky gate on the surface of the heterostructure.

To form nanostructures with sharp electrostatic confinement in the 2D layer, it is necessary to use a relatively shallow 2D layer. The distance between the Schottky gate and the 2D layer should be on the order of or less than the width of the desired confinement potential in the 2D layer. Using shallow 2D layers will help to form ballistic quantum point contacts and create small quantum dots with few hole occupation. We were able to obtain a 2D hole layer at a depth of 120 nm from the surface with a low temperature mobility ($T = 0.35 \text{ K}$) of $\sim 2 \times 10^5 \text{ cm}^2/\text{Vs}$ at a density of $2.8 \times 10^{11} \text{ cm}^{-2}$.

We next used our 120-nm deep 2DHS to fabricate quantum dot devices using surface depletion gates. We observed Coulomb blockade oscillations in transport, demonstrating successful formation of a hole quantum dot. Charge noise prevented tuning of the device to the few hole regime and charge sensing of the dot occupation. Reduction of this charge noise in depletion mode nanostructures will be key to enabling future hole quantum dot experiments.

Significance:

As an investigation of the basic physics of p-type nanostructures, this work will have relevance to DOE's mission of scientific discovery and innovation. Due to the expectation of longer spin coherence times for holes than for electrons in GaAs, this work may provide new capabilities in the area of solid state quantum information processing, a research topic with a variety of potential applications ranging from high-performance computing to secure communications.

Nanofabrication of Tunable Nanowire Lasers via Electron and Ion-Beam Based Techniques

153346

Year 2 of 2

Principal Investigator: Q. Li

Project Purpose:

There is a strong desire to reduce the volume of lasers to the minimum limit in order to enable ultracompact and low-threshold coherent light sources. Such nanolasers could enable a host of impactful and diverse applications such as nanoscale optical interconnects, ultrahigh-density data storage, nanolithography, quantum computing, cell probes, and chem-bio sensing. However, control of the optical emission properties of nanolasers is difficult due to a number of factors, including challenges of controlling nanowire material uniformity, dimensions, and morphology. Additionally, diffractive optical loss in the nanowire cavity creates a limit to the wire dimension to about 150-nm diameter. The desire to realize an electrically injected nanowire laser places an additional constraint on the modal control. We are attempting to achieve loss reduction through modal control using novel distributed feedback schemes onto a single nanowire to achieve low threshold efficient nanowire lasers. We are using high-quality III-nitride nanowire heterostructures with strong mode confinement and novel optical nanocavity design. We are exploring the use of high-resolution electron beams and focused ion beams to fabricate single nanowire lasers directly incorporating distributed feedback (DFB) grating features within or on the nanowire. A novel DFB mechanism, which to our knowledge has never been demonstrated in nanowires, would enable modal control and frequency tuning and would minimize optical losses in GaN nanowire lasers. The DFB nanowire laser device will be designed and fabricated to maximize directional reflectivity and minimize scattering loss. This advance will allow controlled tuning of the nanowire laser emission characteristics independent of nanowire-to-nanowire variations including length and will reduce optical losses from the nanowire end facets, laying the groundwork for future electrically injected nanowire lasers.

Summary of Accomplishments:

We have demonstrated GaN nanowires with precisely controlled geometry that showed single-mode lasing with optical pumping. Control of the GaN nanowire geometry is realized by a top-down technique, which combined a lithographically defined dry etch followed by a tunable anisotropic wet etch. The resulting GaN nanowires are m-plane bounded with tightly controlled diameter and length. Single-mode lasing is indicative of high optical gain and narrow gain bandwidth achieved in the GaN nanowires because of high material quality. GaN nanowires, each with 130 nm diameter and 5 μm length, show single-mode lasing, over a wide excitation range, with line width of ~ 0.12 nm and threshold of ~ 300 kW/cm². Numerical simulations based on a multimode laser theory indicate that the suppression of transverse and longitudinal side-modes is caused by strong mode competition and narrow gain bandwidth. Moreover, stable single-mode lasing operation from a pair of coupled GaN nanowires has been demonstrated through optical pumping. The GaN nanowires with different length were placed in contact to form a coupled cavity through nanoprobe manipulation. Unlike individual nanowire lasers, which operate in a combined multiple transverse and multiple longitude mode oscillation, a coupled nanowire provides a mode selection mechanism through Vernier effect, which can strongly enhance the free spectrum range between adjacent resonant-modes and generate a stable single-mode operation with a high side mode suppression ratio. We also demonstrated a method for mode-selection by coupling a GaN nanowire laser to underlying gold substrates. Multi-mode lasing of GaN nanowires is converted to single-mode behavior following placement onto a gold film. Simulations show that a mode-dependent loss is generated by the absorbing substrate to suppress multiple transverse-mode operation with a concomitant increase in lasing threshold of only $\sim 13\%$. This method provides greater flexibility in

realizing practical single-mode nanowire lasers and offers insight into the design of metal-contacted nanoscale optoelectronics.

Significance:

This project resulted in new capabilities and understandings of how to create and control the emission properties of single nanowire lasers. It also helps pave the road for realizing electrically injected nanowire lasers at Sandia. Tunable nanowire lasers will significantly impact DOE and Sandia national security missions by enabling an ultracompact, low-threshold, coherent ultraviolet-visible light source that could be integrated into numerous nano-and microsystems such as atom-chip sensors. New functionalities will be enabled in the integration of electronics and photonics, chem-bio detection and sterilization, solid-state lighting, ultrahigh-density storage, and high-resolution imaging and lithography.

Refereed Communications:

Q Li, J.B. Wright, W.W. Chow, T.S. Luk, I. Brener, L.F. Lester, and G.T. Wang, "Single-Mode GaN Nanowire Lasers," *Optics Express*, vol. 20, pp. 17873-17879, 2012.

Q. Li, K.R. Westlake, M.H. Crawford, S.R. Lee, D.D. Koleske, J.J. Figiel, K.C. Cross, S. Fatholouloumi, Z. Mi, and G.T. Wang, "Optical Performance of Top-Down Fabricated InGaN/GaN Nanorod Light Emitting Diode Arrays," *Optics Express*, vol. 19, pp. 25528-25534, December 2011.

Time-Resolved Chemical Mapping of Phase Transformations in Li-ion Battery Electrodes

153892

Year 2 of 2

Principal Investigator: J. D. Sugar

Project Purpose:

In order to make battery technologies a more attractive energy storage alternative to carbon-based fuels, we must increase their capacity, charge/discharge rates, and improve safety. All of these performance criteria are limited by the answer to this question: what controls how the ionic charge carriers enter and leave the electrodes? Although electronic and ionic conductivities are an important part of answering this question, equally important considerations are the rate-limiting steps in the electrode phase transformations. These de/lithiation reactions involve a structural transformation that could be limited by diffusion, surface-attachment, or strain. To date, these electrode reactions have mostly been investigated ex situ, and the intermediate steps must be interpolated from available data. An in situ observation of the transformation provides the missing information but requires complex sample preparation techniques and a quantitative analytical approach for observing Li^+ ions to determine definitively which mechanisms dominate the charge storage dynamics. To differentiate between the different possible dominant mechanisms, we will develop an in situ analytical capability in the transmission electron microscope (TEM) and a thin-film battery design so that the microscopic details of the phase transformation can be observed while they occur. This work develops a capability to perform analytical energy-filtered TEM (EFTEM) in situ, which allows quantitative chemical measurements of battery electrode reaction kinetics at the nanoscale. This work also develops a thin-film battery platform that can be cycled inside the TEM by applying a bias without the need for a special environmental cell. These two activities combined create high-risk, cutting-edge work that has the potential to significantly advance the current understanding of how to optimize battery electrode materials for higher capacity, charge/discharge rates, and safety.

Summary of Accomplishments:

We developed a quantitative TEM-based spectroscopy technique that allows us to map the oxidation state of Fe in LiFePO_4 battery electrodes. This technique uses a parallel electron beam rather than a focused one and is novel because it does not introduce damage into the sample. Other TEM techniques alter the oxidation state of Fe during the observations. We also developed a sample preparation technique based on ultramicrotomy that allows us to make serial thin cross sections of an entire battery electrode. As a result we can analyze the Fe oxidation state and morphology of an entire section of battery electrode particle-by-particle. This new capability utilizes a well-established technique (ultramicrotomy) in a new way. We are not aware of any other researchers who have used ultramicrotomy in this way. We validated our spectroscopic TEM measurements with spectroscopic measurements on the scanning transmission x-ray microscopy (STXM) (synchrotron-based) and confirmed that our technique gives the same answer. We demonstrated that we can combine synchrotron and TEM-based measurements on the same exact samples to learn more about the system than the individual techniques would have given by themselves. This combination of techniques is at the forefront of state-of-the-art characterization. We analyzed many particles in a single battery charged to 50% state of charge and learned that the phase transformation kinetics are completely limited by the nucleation of new phases. We developed a simple phenomenological model that explains our observations.

Significance:

In alignment with the DOE mission of scientific discovery and innovation, our results advance the frontiers of science because of the new capabilities we have developed. We have pushed the limits of electron microscopy by developing a spectroscopic technique for measuring Fe oxidation state and reduced artifacts that result from beam damage. We have also developed a sample preparation technique that does not alter the microstructure of samples and produces high-quality, thin samples for analysis at the nanoscale. This technique is completely general for any type of polymer composite material. We are now in a position to develop models to understand how to improve battery technology.

On-Chip Low Power Frequency Comb with Spectral Selectivity 154081

Year 2 of 2

Principal Investigator: R. Camacho

Project Purpose:

On-chip wavelength division multiplexed (WDM) networks for next-generation ExaFLOP computing and optical interconnects lack efficient “optical power supplies” for the thousands of laser frequencies needed. Millimeter-wave (100 GHz) sensors and secure communications approaches lack small, low-power means of generating the required complex waveforms. Ultrafast optical switching and logic remains a “science project” due to lack of a viable micro-integration path. This project has laid the foundation to address these needs by leveraging Sandia’s silicon photonics platform to bring nonlinear optics to the chip-scale.

In this work, we have developed a simulation and fabrication toolset that use optical nonlinearities (four-wave mixing) in silicon nitride for on-chip, low power, ultranarrow line-width frequency combs compatible with complementary metal-oxide-semiconductor (CMOS) processing. This chip-scale comb-generator converts single-frequency input laser light into an array of equally spaced laser wavelengths that in future implementations can be routed and processed by on-chip WDM networks or used in ultrastable (fsec) timing sources, fast spectroscopic sensors, and arbitrary RF-photonics waveform generators. We have integrated new insights in multifrequency selective high-Q resonators and developed the theoretical and simulation toolset to demonstrate chip-scale 40+ line comb generation.

Summary of Accomplishments:

- We have built a complete multiphysics simulation toolkit demonstrating exactly how the mutual coherence of the comb-lines builds up and leads to a coherent output.
- We have identified novel ways to tailor the geometric and material dispersion characteristics of resonator that allows for both energy and momentum conservation across a large bandwidth. In the process, we have determined the role of both direct and cascaded nonlinear processes in the overall coherence properties of the comb.
- We have derived an expression for the quantum mechanical bi-photon wave function and spectra resulting from four-wave mixing in an azimuthally symmetric optical resonator. The existence of two “special” modes have been identified that conserve both energy and momentum far outside the bandwidth of the angular group velocity dispersion walk-off. It is anticipated that such a device may find use in the practical generation of widely separated narrow-band entangled photons.
- The state-of-the art optical materials used in microscale comb generation have a fundamental trade-off: low-loss is achieved at the expense of high optical nonlinearities. We have identified a far more “ideal” material that minimizes this tradeoff.
- We have proposed that the dynamics of comb generation may be enhanced in magnetically active materials. Specifically, we suggest that active gyrotropic control of the comb center frequency can provide a way to stabilize the comb output without changing the pump power or frequency. Furthermore, we have outlined a concept for the first-ever robust microscale distributed magnetometer based on frequency combs.
- Finally, we have succeeded in demonstrating a novel fabrication technique that completely overcomes the deleterious effects of stress in thick silicon nitride films. Using the new process, we have grown thick (> 750 nm) layers of stoichiometric silicon nitride with no cracking or stress-induced deformations.

Significance:

In the field of silicon photonics, on-chip optical signal generation is the final step to “untethering” chip-scale optical processing from bulky power supplies and laser sources for truly hand-held, low-power applications. It would displace the need for tens of off-chip lasers for wavelength division multiplexing, instead allowing for the generation of optical signals in an integrated platform. Other applications include light-detection and ranging (LIDAR), global positioning system (GPS), handheld pico- and femto-second pulse generation for applications like simultaneous ballistics testing/detonation and high-speed synchronous cameras, miniaturized spectroscopy, microscale molecular fingerprinting, advanced optical coherence tomography, quantum communications, and many others, thus showing application in multiple DOE and DHS missions.

Refereed Communications:

R.M. Camacho, “Entangled Photon Generation using Four-Wave Mixing in Azimuthally Symmetric Microresonators,” *Optics Express*, vol. 20, pp. 21977-21991, September 2012.

On-Chip Coherent Qubit Operations with Microfabricated Surface Ion Traps

154195

Year 2 of 3

Principal Investigator: C. Highstrete

Project Purpose:

Trapped atomic ion quantum bits (qubits) have been employed successfully for quantum information (QI) processing and are promising for quantum computation. Primarily, tightly focused laser beams have been used to address electronic energy levels of individual ions (single qubit operations) and motional modes of qubit subsets (multi-qubit entangling operations). However, spontaneous emission and technical difficulties stabilizing laser frequency, phase, amplitude, and beam pointing have kept fidelities below fault tolerant levels. Alternatively, microwave fields can be used to manipulate ion qubits based on the hyperfine-split electronic ground state. Such qubits portend higher fidelity because they are practically immune to decoherence by spontaneous emission and are readily addressed by highly stable microwave components. However, limited utility has been realized with these qubits because, for free space microwaves, 1) the long wavelength precludes focusing, causing all qubits to be simultaneously addressed and 2) small field gradients on the atomic scale produce negligible coupling to motional modes. Utilizing state-of-the-art microfabrication techniques, microwave electrodes with subwavelength dimensions can be designed to localize fields and generate high magnetic field gradients to individually address qubits (by selective frequency shifting) and excite motional modes. In this project, we will design and integrate sub-wavelength microwave electrodes into ion trap chips and perform local single- and two-qubit coherent operations. While Sandia's Microsystems and Engineering Sciences Applications (MESA) facility is the world leader in surface ion trap microfabrication technology, a critical next step is to perform coherent trapped-ion qubit operations. Sandia is uniquely poised to make a game-changing revolution by developing and demonstrating on-chip, localized, and laser-less qubit operation technology.

Solar Fuel Cell for Photocatalysis of Organic Pollutants with Simultaneous H₂ Production

155797

Year 2 of 3

Principal Investigator: K. R. Reyes

Project Purpose:

The purpose of the project is to develop nanostructured WO₃/TiO₂ composite nanotubes with enhanced properties to drive solar photoconversion reactions, including photodegradation of organic pollutants and solar water splitting. The use of sunlight to split water is one promising possibility of storing solar energy in an energy carrier (hydrogen) to allow storage and distribution. For solar-to-hydrogen conversion, specialized semiconductors are needed to absorb sunlight and use this energy to produce clean hydrogen. Metal oxides are good candidates because of their good photocatalytic activity, but their efficiency is jeopardized by three important factors: 1) poor charge-carrier mobility, 2) large bandgaps (E_g), and 3) fast electron/hole recombination. This project will focus on the manipulation of semiconductors to correct each of those limiting factors in comprehensive and synergistic approach. We are proposing to develop organized composite WO₃/TiO₂ nanostructures to direct the flow of photogenerated charges more efficiently than nanoparticle networks, for instance. In addition, aqueous organic pollutants will be used as hole scavengers to reduce the electron/hole recombination in the photoanode and consequently increase the hydrogen production in the cathode. The TiO₂ nanotubes have been prepared by anodization of Ti foil and used as “skeleton” for WO₃ electrodeposition. Scanning electron microscopy (SEM) results indicate that this composite WO₃/TiO₂ has the same ordered structure as TiO₂ nanotubes with an external WO₃ layer. Diffuse reflectance spectra show an improvement in the visible absorption relative to bare TiO₂ nanotubes and in the UV absorption relative to bare WO₃ films. Incident photon to current efficiency (IPCE) increased from 30% (for bare WO₃) to 50% (for WO₃/TiO₂ composites) and extended up to the visible region (575 nm). With the addition of methanol (organic pollutant model) the photocurrents exhibited more than five-fold increase. This innovative photoelectrochemical system would have a high potential for clean hydrogen production as well as pollutant photodegradation treatment.

Beyond the Ideal Nanostructure: Local Environmental Effects on the Electronic and Optical Properties of Carbon Nanotubes

157694

Year 2 of 3

Principal Investigator: D. C. Spataru

Project Purpose:

In this project, we are theoretically addressing how a metallic substrate impacts the electronic and optical properties of carbon nanotubes. Employing ab initio methods that take into account many-electron correlation effects, we plan to study two cases: 1) nanotube interacting with a non-structured metallic surface and 2) nanotube in resonance with plasmonic materials. Including many-electron effects through ab initio calculations is computationally very demanding. The groundbreaking calculations we are attempting are especially challenging because the nonperiodic nature of the systems requires large-size supercells to accommodate complex many-electron correlation effects.

To overcome these challenges, we have developed a new embedding approach that goes beyond standard ab initio many-electron approaches, in which polarization effects from the substrate/plasmonic material are effectively included by properly renormalizing the Coulomb interaction between electrons in the carbon nanotube (CNT). We have benchmarked our embedding approach (against full ab initio calculations and experiment where available) for the case of the benzene molecule on a metal surface. We have also applied the embedding approach for the case of a semiconducting carbon nanotube on an Au surface and have obtained very good agreement with experiment. Our calculations reveal the important role played by the intrinsic dielectric properties of the carbon nanotube in renormalizing energy levels in the presence of the metallic substrate.

We are preparing two manuscripts based on the results of the calculations of benzene/carbon nanotube on a metallic surface.

We have also adapted our embedding approach for the case where energy levels in the nanotube are resonating with surface plasmons in a plasmonic material. Next, we will apply the embedding approach to the calculation of bandgap renormalization, photoabsorption rates, and exciton radiative lifetime in a CNT placed in the proximity of a plasmonic material.

Micro-Scale Heat Exchangers for Cryogenic Micro-Cooling Applications 158181

Year 2 of 3

Principal Investigator: A. J. Gross

Project Purpose:

There is a need to create new microscale heat exchanger structures, which can be used to implement cryogenic cooling of low-power microelectromechanical systems (MEMS) and microelectronic devices. Development of high-performance microscale coolers will enable high-performance cryogenic sensors and electronics to be deployed in systems where their size and power consumption are currently prohibitive.

Cryogenic coolers capable of reaching temperatures of 100 K or lower often rely on Joule-Thomson (JT) or Stirling cycle cooling. Both types of devices require efficient heat exchangers. However, previous micro-JT and micro-Stirling coolers suffered from parasitic heat losses resulting from the fabrication techniques and materials used. Additionally, many of these devices have not been compatible with wafer-scale integration. The current state of the art has, therefore, failed to address the need for a highly integrated and efficient solution to cryogenic cooling at the microscale. The proposed work will address this problem through the development and demonstration of new structures that implement micro-fabricated heat exchangers for use in microscale coolers.

This project is focused on implementing counter-flow heat exchangers (CFHXs) that have high efficiency and can be integrated into complete systems. This project is differentiated from previous work by focusing on planar, thin film micromachining instead of bulk materials. A process is under development for fabricating coaxial fluidics using thin film dielectrics. The use of thin film dielectrics provides thermal isolation, increasing efficiency of the coolers compared to designs based on bulk materials, and it will allow for wafer-scale fabrication and integration. The process will be used to demonstrate a CFHX as part of a J-T cooling system for applications with heat loads less than 1 mW.

New Thin Film Materials for Electronics

158184

Year 2 of 2

Principal Investigator: A. M. Schwartzberg

Project Purpose:

This project is developing and investigating novel thin film organic conductors with drastically improved electronic properties over the current state of the art. By leveraging the unique crystallinity of metal-organic frameworks (MOFs) and a novel Langmuir-Blodgett deposition technique, we are attempting to generate large area crystalline organic films for electronic applications on any substrate. We are developing a new set of characterization tools by both building up capability at Sandia and through the user facility at the Molecular Foundry at Lawrence Berkeley National Labs (LBNL). We also are developing a synthetic methodology for the growth of large area crystalline thin films of MOFs, currently impossible, and a set of imaging and spectroscopic tools including confocal and near-field Raman imaging, atomic force microscopy, electron microscopy, and scanning transmission x-ray microscopy, revealing ultrahigh-resolution chemical information critical to a complete understanding of film growth kinetics. While this technique and the resulting materials will be fundamentally different from current crystalline thin-films, many of the underlying questions remain the same: What is the nature of nucleation and how does it affect overall growth? How do defects form and propagate through the film? It is conceivable to propose mechanisms similar to those in ionic crystal growth such as catalytic nucleation, and lattice vacancies. We are using our expertise in spectral imaging and synthetic nanochemistry to answer these and other questions, and apply the results to improve materials growth.

Summary of Accomplishments:

In collaboration with the Molecular Foundry at LBNL, a Langmuir-Blodgett trough (LB) was built from scavenged parts and added to a scanning Raman microscope at LBNL. Because MOF thin film growth efforts begin very slowly, existing peptoid sheets were used as surrogates to test system capabilities. These are lipid bilayer like structures composed of engineered peptoid monolayers. The test results showed that it is possible to not only measure Raman of individual peptoid sheets, but also successfully perform full hyperspectral Raman imaging. We observe signature Raman modes from the substituent molecules, and even see regional variation in those signatures indicating some level of structural inhomogeneity. These are the first results to demonstrate confocal Raman imaging of a single peptoid sheet. They are also the first to demonstrate near-field photoluminescence imaging of peptoid sheet at less than 70-nm resolution. In addition to Raman imaging, preliminary tests also demonstrated the super-resolution imaging of a peptoid sheet with an integrated dye molecule. This work seems to indicate that there are crystalline domains present within the sheets, something predicted, but never observed. This will be pursued in future studies.

MOF thin films present great potential for revolutionizing solid state bulk- and nano-scale device physics. This work has helped position Sandia for advance in this area of MOF film creation. The interactions with LBNL also led to award of two user projects at the Molecular Foundry at LBNL led by current Sandia staff and the appointment of a current Sandia staff to the Molecular Foundry User Executive Committee.

Significance:

The results showed that a single peptoid sheet can be successfully imaged using confocal Raman spectroscopy and a peptoid sheet can be successfully imaged using near-field photoluminescence at a resolution less than 70 nm. These results have positioned Sandia for advance in this area of MOF film creation and advance the DOE mission in of scientific discovery and innovation.

Cubic Organic Scintillators as Improved Materials for Fast Neutron Detection

158481

Year 2 of 3

Principal Investigator: P. L. Feng

Project Purpose:

The purpose of this project is to develop improved fast neutron scintillators through rational design of the crystal structures of organic materials. Crystalline organic scintillators are the best materials for fast neutron discrimination and spectrometry but have several limitations such as brittleness, anisotropic light emission, and finite particle discrimination performance. These considerations are directly controlled by the molecular and crystalline structures via electronic structure considerations and second-rank tensor properties, respectively. Unfortunately, all known organic scintillators crystallize in low-symmetry monoclinic structures, which limits the study and improvement of these fundamental properties. For example, a crucial factor that determines the efficiency of particle discrimination is the triplet mobility within a material. The mobility is directly controlled by the molecular orientations and crystallographic packing structure, neither of which may be varied or systematically understood in existing materials. Low-symmetry crystalline scintillators also suffer from anisotropic optical and mechanical properties that limit their practical use in critical applications such as nuclear nonproliferation.

This work represents the first experimental investigation of the scintillation behavior of high-symmetry organic crystals. Furthermore, the technical approach employed here is one of molecular design, which differs considerably from existing empirical strategies. Instead, eight, high-symmetry organic structures have been successfully synthesized according to an approach that comprises crystal engineering via C3-symmetric molecular structures. Characterization of several of these new scintillators reveals superior scintillation timing and particle discrimination performance relative to their low-symmetry counterparts. In addition to direct relevance towards radiation detection applications, the materials developed in this project have implications for the design of new substrates for improved charge carrier transport in organic photovoltaic applications. Furthermore, theoretical predictions of enhanced diffusion rates and reduced percolation thresholds in high-symmetry organic structures have yet to be explored and confirmed experimentally, which positions this work for significant interdisciplinary impact.

In-situ Study of Dynamic Phenomena at Metal Nanosolder Interfaces using Aberration-Corrected Scanning Transmission Electron Microscopy

158822

Year 1 of 3

Principal Investigator: P. Lu

Project Purpose:

Controlling metallic nanoparticle (NP) interactions plays a vital role in the development of new joining techniques (nanosolder) that bond at lower processing temperatures but remain viable at higher temperatures. The primary objective of this project is to develop a fundamental understanding of the actual reaction processes, associated atomic mechanisms, and the resulting microstructure that occur during thermally driven bond formation in nanoscale (<50 nm) metal-metal interfaces. Current theory describes the formation of bonding at high temperatures based on micron-scale phenomena but nanoscale materials operate in a unique, unknown fashion. The reason for the change in metal-metal interactions is an open question, but understanding this behavior is critical to the development of nanointeractions (i.e., nanosolders) and basic science. This question can only be answered with in situ, atomic-scale dynamic observation, enabled by state-of-the-art heating experiments in the unique, aberration-corrected scanning transmission electron microscope (AC-STEM), coupled with large-scale, high-fidelity molecular dynamic (MD) simulations. This research effort will provide an understanding of nanoscale interface interactions at elevated temperatures and provide science-based solutions that address several near-term, critical Sandia mission needs.

Recent in situ transmission electron microscopy (TEM) efforts have met with limited success due to lack of the specialized equipment necessary to address dissimilar metal interactions. By combining the state-of-the-art AC-STEM and TEM heating stage, NP synthesis expertise, atomic-scale characterization, in situ TEM, and atomic-scale MD modeling, we have a unique opportunity to understand/control complex nanoscale interface interactions. The AC-STEM offers sub-Angstrom (0.8 Å) imaging resolution uniquely coupled with near-real-time element mapping, revealing previously unobservable rapid atomic-scale compositional changes occurring at these nanoscale interfaces at elevated temperatures. Additionally, the in-situ TEM heating holder possesses a fast thermal ramp (~1000 °C/ms) enabling thermally quantized observation of these interactions. The experimental insight provided by in situ, dynamic observations will be coupled with atomic-scale MD modeling, further elucidating the mechanisms of bonding in metal-metal NPs and the influence of physical properties on the reaction mechanism.

Deciphering Adsorption Structure on Insulators at the Atomic Scale

158823

Year 1 of 3

Principal Investigator: K. Thuermer

Project Purpose:

Whether to understand ice-nucleation in clouds, lubricant degradation in micromachines, or aqueous electrochemical kinetics, molecular-level knowledge of water-solid interactions is desirable. Water behavior at interfaces has, therefore, been the subject of hundreds of studies. Still, even the simplest issue, the structure of the first water layer on a solid surface, has been hard to resolve. For three decades, low-temperature, 2D wetting layers on close-packed precious metal surfaces were thought to be “ice-like” arrangements of water molecules, strained into registry. In the past year, via scanning tunneling microscopy (STM) and density functional theory (DFT)-supported interpretation, we overturned that idea, discovering the remarkably non-ice-like molecular arrangement adopted by water on Pt(111). That success offers the prospect of understanding how water binds to the more stable materials: oxides, sulfides, and salts, of which the world is largely comprised. The obstacle is that these materials are generally insulators, for which high-resolution microscopic techniques have been unavailable. Molecular-scale images were indispensable to solving the Pt(111) wetting-layer structure. We can expect that high-resolution imaging will be equally important to understanding water on the more common materials.

By exploiting an atomic force microscopy (AFM) breakthrough, we aim to be the first to perform atomic-resolution studies of adsorbates on insulating surfaces relevant to environmental and technological processes bearing on national needs. Unprecedented resolution has been achieved with a novel tuning-fork type sensor known as “Q-plus.” Proof-of-principle of the Q-plus technique, atomic-resolution AFM of an adsorbed pentacene molecule suggests breakthrough possibilities for molecules on oxides, assuming the technique proves sufficiently robust to provide similarly high resolution images of delicately bonded, adsorbed water, a risky assumption. Our first goals are the wetting of muscovite and kaolinite, oxides ubiquitous in nature, implicated as cloud-seed materials, and subjects of many experimental and theoretical studies with no definitive conclusions. We will attempt to decipher adsorbed water-molecule arrangements by combining atomic-level imaging with DFT-based interpretation.

Crystalline Nanoporous Frameworks: a Nanolaboratory for Probing Excitonic Device Concepts

158825

Year 1 of 3

Principal Investigator: M. D. Allendorf

Project Purpose:

Electro-optical organic materials hold great promise for the development of high-efficiency devices based on exciton formation and dissociation, such as organic photovoltaics (OPV) and organic light-emitting devices (OLEDs). However, the external quantum efficiency (EQE) of both OPV and OLEDs must be improved to make these technologies economical. Efficiency rolloff in OLEDs and inability to control morphology at key OPV interfaces both reduce EQE. Only by creating materials that allow manipulation and control of the intimate assembly and communication between various nanoscale excitonic components can we hope to first understand and then engineer the system to allow these materials to reach their potential. This project is pursuing the following outcomes: 1) develop a paradigm-changing platform for probing excitonic processes composed of crystalline nanoporous frameworks (CNFs) infiltrated with secondary materials (such as a complementary semiconductor), 2) use them to probe fundamental aspects of excitonic processes, and 3) create prototype OPVs and OLEDs using infiltrated CNF as active device components. These functional platforms will allow detailed control of key interactions at the nanoscale, overcoming the disorder and limited synthetic control inherent in conventional organic materials. CNFs are revolutionary inorganic-organic hybrid materials boasting unmatched synthetic flexibility that allows tuning of chemical, geometric, electrical, and light absorption/generation properties. For example, bandgap engineering is feasible and polyaromatic linkers provide tunable photon antennae; rigid 1–5 nm pores provide an oriented, intimate host for triplet emitters (to improve light emission in OLEDs) or secondary semiconducting polymers (creating a charge-separation interface in OPV). These atomically engineered, ordered structures will enable critical fundamental questions to be answered concerning charge transport, nanoscale interfaces, and exciton behavior — properties that are inaccessible in disordered systems. Implementing this concept also creates entirely new dimensions for device fabrication that could improve performance, increase durability, and reduce costs with unprecedented control of over properties.

Electrically Tunable Metamaterials for Agile Filtering in the Infrared

158826

Year 1 of 3

Principal Investigator: I. Brener

Project Purpose:

Multispectral infrared (IR) imaging systems use multiple detector arrays and static filters that increase their weight, cost and complexity. Such systems could be greatly improved through the incorporation of fast, pixilated, electrically tunable filter arrays that are tightly integrated with focal plane arrays.

Previous attempts at tunable IR filters have used Fabry-Perot cavities, photonic crystals, or other multi-stacks in conjunction with MEMS, mechanical or temperature tuning approaches. None of these approaches can provide microscale, thin, high optical performance, and electrically tunable IR filter arrays.

We have recently performed proof-of-concept demonstration of two approaches that could fulfill this promise and bring active filter arrays to a practical implementation within three years. We have shown that the spectral response of infrared planar metamaterials is greatly influenced by coupling to high-mobility electron sheets or intersubband transitions in semiconductor heterostructures, placed within 200 nm of the metamaterial resonators. We intend to extend these concepts to electrically tunable filter arrays in the infrared (mid to long-wave: 3–12 microns) by: 1) optimizing this spectral shift through the use of gated InSb/InAs doped layers and heterostructures of the In-Ga-Al-Sb-As material system and 2) designing, modeling, and fabricating new matched metamaterial nanoresonators that couple efficiently to these heterostructures. Ultimately, we envision a monolithic integration of these III-V based metamaterial filters with III-V based infrared focal plane arrays.

This project combines research in the areas of metamaterials, nanophotonics and semiconductor physics in order to provide a compact solution that will impact many mission areas at Sandia. It plays well into the strengths of Sandia, leveraging investments at Microsystems and Engineering Sciences and Applications and Center for Integrated Nanotechnologies.

Understanding Tantalum Oxide Memristors: An Atoms-Up Approach 158828

Year 1 of 3

Principal Investigator: M. Marinella

Project Purpose:

Dynamic random access memory (DRAM), static random access memory (SRAM), and flash memory technologies are nearing physical scaling limits and are starting to require significant switching energy compared to other components of modern computing systems. A recent International Technology Roadmap for Semiconductors (ITRS) report has determined that memristive (also referred to as redox) memory is one of the two most promising new memory technologies due to its unprecedented scalability, speed, pJ/bit switching energy, endurance, and retention. The report has recommended that the technology receive increased research focus. Government customers have already invested in memristor technology for national security applications and as a rad-hard memory. However, current state of the art memristors continue to exhibit serious uniformity and reliability problems; for example, resistances can vary by several orders of magnitude for devices within the same array. Industry is using Edisonian approaches to these problems, resulting in slow, incremental progress. The physical mechanisms enabling switching between high- and low-resistance states are thought to involve the motion of oxygen vacancies in a region that is only tens of nanometers thick. However, we still cannot definitively answer the question — what is moving where, and how? Thus, the central scientific problem is to identify the physical and chemical changes responsible for resistive switching. This will enable us to engineer reliable devices with predictable electrical behavior. Memristors present Sandia with a time-sensitive opportunity to achieve this understanding and significantly advance the field of microelectronics as a whole, while enabling important government applications.

Industry has favored trial and error experimental approaches that often result in minor, incremental improvements. We propose a scientific approach using novel lateral structures to perform a set of linked experiments that results in a physical model of memristor switching. A comprehensive scientific model of this phenomenon will result in a groundbreaking advancement of this technology for both commercial and government applications.

Understanding and Exploiting Bilayer Graphene for Electronics and Optoelectronics

158829

Year 1 of 3

Principal Investigator: S. W. Howell

Project Purpose:

Bilayer graphene (BLG) offers advantages that its more common form, monolayer, does not. Most prominently, a dynamic, “tunable” bandgap can be readily induced in BLG using electrical fields. Understanding this tunability presents a significant scientific challenge that could enable new, potentially disruptive, graphene devices as are envisioned by the latest International Roadmap for Semiconductors. A lack of fundamental understanding, however, has limited the realization of advanced BLG devices. For example, graphene’s electronic properties are exceptionally sensitive to the materials surrounding it in a device. Additionally, there is limited understanding of the factors determining the magnitude and uniformity of the induced bandgap. In response, this project leverages our capabilities in BLG synthesis, characterization, device fabrication, and modeling in order to fundamentally understand BLG properties, thereby providing a scientific foundation for future graphene electronics and optoelectronics.

This project aims to understand the following: 1) the interaction between BLG’s two-dimensional (2D) charge carriers and the metals/dielectrics intrinsic to device integration and 2) the many-body electronic and optical properties of the system. This understanding will allow us to demonstrate a gated BLG device having the potential for disruptive capabilities in electronics and as an infrared detector. The project operates with the belief that BLG is the best platform to study these phenomena and has the greatest promise to fully leverage graphene’s inherent advantages. Most importantly, BLG exhibits a tunable bandgap when exposed to a transverse electric field. There has been no definitive realization of scalable BLG devices, however, due to the limited availability of the material itself and an incomplete understanding of how integration processes alter graphene’s properties. Utilizing our differentiating competency to produce large-area, high-quality, BLG combined with our ability to fabricate, characterize, and model these structures, we are uniquely positioned to address these problems and establish Sandia as the “go to” national resource for graphene nanoelectronics.

GaN Unipolar Optical Modulators 158830

Year 1 of 3

Principal Investigator: G. A. Vawter

Project Purpose:

The purpose of this project is to create a new class of optical data modulator with high bandwidth operation at high temperature in order to bypass the limitations of existing modulator technology. Conventional optical modulators change transmitted light intensity by modulating the interband (electron to hole, e-h) absorption energy and are made from InGaAsP/InP materials at telecom wavelengths ($\sim 1.5\ \mu\text{m}$). The small bandgap, long carrier-recombination lifetime, and smearing of the e-h energy separation versus carrier density limit the operating temperature, saturation power and recovery time of the modulation. We are using the extremely fast phonon-assisted relaxation times ($\sim 100\ \text{fs}$) and the high density-of-states of the intersubband (ISB) transitions (electrons in the conduction band) in GaN/AlN quantum well (QW) structures to improve saturation power, recovery from saturation, and operating temperature in optical intensity modulators operating at $\sim 1.5\ \mu\text{m}$.

In this first year, we have demonstrated $1.5\text{-}\mu\text{m}$ ISB absorption transitions with an 86-meV line-width in AlGaIn/AlN QWs. Physics models of ISB transitions in III-As-P materials were developed to include the polarization fields present in III-nitride materials and refined based on experimental absorption data. Using these we have invented a new QW design with field-induced ground state splitting. The new QW approach has become our baseline design as it modulates the ISB absorption on and off without large changes in energy levels and at reduced electric field, offering a 10X reduction in applied voltage versus single QW designs.

Additionally, we have demonstrated the first ion-implant-induced quenching of the ISB absorption, paving the way for integration of modulators with non-absorbing interconnect waveguides. Finally, we have fabricated initial optical waveguides of AlGaIn/AlN and characterized their optical transmission.

Intrinsically Radiation-Hard Nonvolatile Memory: SnO₂ Memristor Arrays

159056

Year 1 of 3

Principal Investigator: E. J. Garcia

Project Purpose:

We propose to investigate SnO₂-based memristors to create inherently radiation-hardened, ultradense, non-volatile memory (NVM). Radiation-hardening-by-design is an effective solution, which is based on redundancy and implemented in layout and architecture; however, it comes with the penalties of strict design constraints, lower performance (>1 Moore's Law generation) and higher cost (10,000 times more expensive than its commercial counterpart). An inherently radiation-hardened, ultradense, nonvolatile memory device compatible with complementary metal oxide semiconductor (CMOS) is key to relaxing design constraints and accelerating progress in radiation-hardened CMOS.

The memristor is a new type of memory device that has the potential to combine the best characteristics of the hard drive, random access memory (RAM) and flash in terms of density, access speed and power, and resistance to radiation effects. Excellent switching times of ~10 ns, memory endurance of >10⁹ cycles, and extrapolated retention times of >10 years have been reported. Importantly, memristors are inherently radiation-hardened since information is stored as a structural change and not as electronic charge. Although different material systems have been investigated for memristors, SnO₂ has received little attention even though it is resistant to displacement and ionizing damage and has excellent electronic properties. Furthermore, SnO₂ can be deposited on flexible surfaces.

This project builds on relevant work and technologies, and US-Mexico collaborations to make a unique and inherently radiation-hardened NVM based on SnO₂ memristors. The project will combine the intrinsic radiation resistance of both the memristor structure and SnO₂ to make inherently radiation-hardened NVM. SnO₂-based memristor memory arrays will be fabricated on silicon wafers and tested for radiation hardness for the first time. Standard CMOS input/output (I/O) electronics and microsystems will be integrated with the memristor arrays to show NVM functionality. Moderately complex functionality of pre- and post-irradiated memristor arrays with peripheral electronics will be demonstrated. The work is a collaboration with the University of Texas at El Paso.

Measuring the Microscopic Mechanics of Individual Intermolecular Systems 159167

Year 1 of 2

Principal Investigator: R. W. Friddle

Project Purpose:

The mechanical properties of materials, both within their bulk and at their interfaces, are ultimately decided by the inter-atomic potentials between neighboring molecules. In composite and smart materials, a degree of complexity is inherent due to the integration of typically organic fibers with inorganic metals or ceramics. Simplification of these systems is found through investigating key properties, such as bond breaking, configurational changes, and elastic deformations at the single molecule level. Understanding the microscopic mechanics of individual molecules is critical to connect the properties of bulk materials with the molecules from which they are composed. However, techniques that can access these properties are scarce, leaving the accuracy of computational calculations to only be validated through indirect means. To bridge this gap, we propose an advanced approach to investigate intermolecular bonding by mechanically probing single molecules with subnanometer spatial and piconewton force resolution.

This project is developing a unique and powerful technique to experimentally reconstruct free energy landscapes of intra- and inter-molecular bonds that compose functional materials and devices. The technique is based on existing atomic force microscope (AFM) technology used in force measurement mode, which typically relies on relatively flexible cantilevers that easily snap in and out of contact with the sample, and is plagued by tip-sample drift. Our technical approach is aimed at improving two aspects of force measurements by AFM: 1) prevent snapping instabilities to allow probing of the full interaction profile and 2) eliminate tip-sample spatial drift along the x, y, z axes to allow fully equilibrated, controlled manipulation of the interacting molecules. Using stiff cantilevers and sampling at high acquisition rates will circumvent the first of these, using an external system. The second problem will be addressed by employing a novel double-cantilever scheme that eliminates x-y drift while allowing controlled relative z-displacement.

Coupling of Quantum Dots to Nanoplasmonic Structures

159184

Year 1 of 3

Principal Investigator: I. Brener

Project Purpose:

The goal of this research is to investigate coherent amplification of subwavelength surface plasmons in quantum-dot lasers, in collaboration with New Mexico State University. Quantum-dot lasers are extremely attractive because of their compact size, high spectral selectivity, ultralow power consumption, higher gain, and increased modulation bandwidth. To fully exploit the unique properties of quantum dots, such as atomic-like spectra, ultrahigh charge carrier concentrations, and wide spectral tunability via the quantum size effect, it is crucial to maximize light-quantum dot interaction. Due to the diffraction limit of traditional optical systems, light confinement comparable to the physical size of quantum dots is extremely difficult. In addition, integration of quantum dots into a stable optical cavity is a major technical challenge in nanophotonics. This research will address these technical challenges of quantum-dot lasers by creating novel plasmonic nanocavities integrated with highly stable giant nanocrystal quantum dots (g-NQDs).

The project is investigating optical gain and stimulated emission profile of optically pumped quantum-dot plasmon nanolasers. The proposed nanolaser utilizes distributed feedback of deep subwavelength plasmon-polaritons in a periodically coupled plasmonic nanocavity to amplify the stimulated emission of embedded quantum dots. To our knowledge, amplification of stimulated emission profile via distributed plasmonic feedback was not reported in open literature. The proposed approach will provide a coherent, ultralow power, and narrow line-width optical source. The impact of this research is broad since the proposed laser can provide a novel highly coherent nanometer scale optical source for fundamental scientific research as well as various applications, such as sensing and communications.

Calculation of Nucleation Pathways in Membrane Systems 159185

Year 1 of 1

Principal Investigator: A. Frischknecht

Project Purpose:

Soft condensed matter systems consist of molecules that self assemble into complex mesoscopic structures. These systems are easily deformable by external stresses, including thermal fluctuations, and can therefore undergo many interesting phase transitions as nucleated (rare) events. We will address the difficult problem of nucleation in soft condensed matter, with a particular focus on biomembranes.

Conventional molecular dynamics simulations attempt to overcome the long timescale challenge by setting up the system in such an unstable state that the phase transition occurs instantaneously. The potential of mean constraint force method can be applied to study a phase transition as a nucleated process. The method requires artificially selecting a reaction coordinate constraint that, in general, may not coincide with the true transition pathway involving the many degrees of freedom of the molecules. Furthermore, the system is limited by the number of molecules that can be simulated and suffers nontrivial system-size effects. Another approach is to develop simpler molecular models and to apply Monte Carlo or density functional methods. However, the interpretation of structures comparable to the molecular size is highly problematic for these overly simplified models. Obviously, the current methods are insufficient for addressing the nucleation question in these complex systems.

We will, in collaboration with the California Institute of Technology (Caltech), develop a method that allows us to study the full minimum energy path (MEP) by combining the string method with dynamic self-consistent field (DSCF) theory. Mathematicians developed the string method for the study of rare events. The method assumes a well-defined free energy landscape that does not exist for most real systems. We overcome this by computing the free energy surface “on the fly” using DSCF theory.

Our method opens the way to studying a wide range of membrane nucleation phenomena, including those involving nanoparticles. This will provide valuable insight towards understanding the toxicity of nanoparticles, guiding gene/drug delivery and understanding the mechanism of endocytosis.

Summary of Accomplishments:

Within self-consistent field theory, we developed an “on-the-fly” string method to compute the minimum free energy path for several activated processes involving a charged, solvophobic nanoparticle and a lipid membrane. Under tensions well below the mechanical stability limit of the membrane, and in the regime where nucleation can occur on experimentally relevant time scales, our study shows that there can be at least three competing pathways for crossing the membrane: 1) particle-assisted membrane rupture, 2) particle insertion into a metastable pore followed by translocation and membrane resealing, and 3) particle insertion into a metastable pore followed by membrane rupture. In the context of polymer-based gene delivery systems, this suggests a novel role of the particle in the endosomal escape, not previously envisioned.

For particle-assisted membrane rupture, a key consideration is the membrane structure at the transition state, which is primarily controlled by the membrane tension. In particular, the membrane tension must be sufficiently high, so that the size of the critical nucleus is on the order of the particle radius. Once this criterion is met, the charges on the particle are enough to promote the adsorption onto and subsequent puncture of the membrane but not so much as to stabilize the pore. In the case of particle translocation, increasing particle charge increases the barrier because the particle gains more favorable

electrostatic interactions by adsorbing onto the surface of the membrane rather than inserting into a pore. In contrast, increasing particle solvophobicity decreases the barrier because the particle inserted into a pore can interact favorably with the hydrophobic lipid tails. With sufficient tension, the pore with a particle inserted into the center of the membrane becomes a metastable state. Finally, we found another nucleated pathway from this metastable state: pore expansion, leading to rupture.

Significance:

For the specific problem of nanoparticles crossing membranes, the types of calculations performed here can be used to identify the optimal conditions for selecting a particular pathway. This would enable engineering of, for example, drug delivery systems, enhancing national security against biological threats, of interest to DHS, and possibly DTRA.

More generally, the methodology developed in this work represents the most advanced theoretical technique for describing nucleation pathways in soft condensed matter systems. We expect the method to be useful for studying a wide range of nucleation phenomena, and therefore enable fundamental science beneficial to the nanoscience, soft matter, and nanoscience communities, including DOE's Office of Science.

Applications of Microwave Frequency Nano-Optomechanical Systems: Oscillators, Circuits, and Sensors

159256

Year 1 of 3

Principal Investigator: M. Eichenfield

Project Purpose:

Nano-optomechanical Systems (NOMS) can simultaneously localize optical photons and microwave-frequency phonons to volumes thousands of times smaller than the volume of the smallest human cell — volumes limited only by the diffraction of the two waves. At this level of localization, the light-matter interaction becomes almost unimaginably strong, with each photon exerting forces on the matter containing it larger than 10 times the weight of that matter. This enables a fully engineerable and scalable platform for light-matter interactions with strengths previously attainable only when trapped atoms, trapped ions, and quantum dots interact with light from external, macroscopic cavities. We are broadly investigating novel NOMS-based chip-scale devices as next-generation acousto-optic circuits for the manipulation and processing of information on the surface of a microchip, as well as using NOMS to develop acousto-optic transducers with unprecedented sensitivity and resolution. In addition, we are discovering many applications of NOMS relevant to ongoing projects at Sandia and the overall mission goals of the DOE.

One major thrust is optomechanical and acousto-optic interactions in aluminum nitride radio-frequency (RF) electromechanical resonators, which are currently fabricated at Sandia. Optical probing provides a completely independent transduction and sensing mechanism in these systems, which will revolutionize the characterization of the devices and yield massive improvements in their operation, as well as provide totally new functionality for acousto-optics.

Another major thrust is optomechanics in nanoscale suspended resonators. These devices promise to be the most sensitive atomic force microscopes (AFM) ever made, as well as eliminating the need for alignment in AFM systems. In addition, they can be massively parallelized using wavelength division multiplexing techniques to make dense linear arrays of AFMs that read out simultaneously and independently to increase throughput by orders of magnitude.

The PI is a President Harry S. Truman Fellow.

Superconductive Silicon Nanowires using Gallium Beam Lithography 159300

Year 1 of 2

Principal Investigator: M. D. Henry

Project Purpose:

The purpose of this project is to combine several recent technological discoveries involving the extremely narrow Ga beam from a Focused Ion Beam Tool (FIB) for implantation of Ga into silicon. These very narrow implantation patterns enable a method for fabricating suspended nanowires (NW) using a completely dry lithographic method as well as superconductive films embedded in silicon; combined, they offer the potential for a writable superconductive NW with better than 3 nm precision. The advantages of the method proposed here is that this fabrication sequence will provide a method to integrate a superconductor, for convenient 4 K liquid He temperatures, using a complementary metal oxide semiconductor (CMOS)-compatible direct-write technology. This method also enables a technological path towards achieving quantum phase slips in nanowires with uniform temperature distribution. Achieving this technology could permit a Josephson Junction replacement technology for the extreme nanoscale limits.

Recent research shows that FIBs can accomplish precision gallium ion implantation into silicon, taking advantage of the highly collimated, sub-3-nm beam widths. This implantation method enables new lithographic techniques for fabrication of electrically conductive NW down to 40-nm diameters and up to 16 microns in length. Other relevant research shows that by saturating a Si wafer with implanted Ga, a thin embedded surface film can achieve type II superconductivity at approximately 7 K.

To date, this project has created fully suspended 10 μm by 30 nm silicon NW. Although these wires have a temperature distribution across the wire unsuitable for superconductivity, we have established a method that will eliminate all temperature gradients across the wire. We have also been able to utilize the suspended NWs as pirani vacuum gauges, thereby significantly reducing size and complexity of the gauge for hermetic and vacuum packaging technology. We have also observed indications of superconductivity in these thin films, although the results are not conclusive.

Two-Dimensional Coupling of Modes Modeling for Spurious Response Prediction in Microresonators

162036

Year 1 of 1

Principal Investigator: R. H. Olsson

Project Purpose:

Microresonators are miniature acoustic resonators that are produced using microfabrication techniques. Because of their small size, frequency diversity, and integration with transistor electronics, microresonators enable frequency agile radio frequency (RF) front-ends for next generation cognitive radios. When realizing microresonator-based filters, one of the largest challenges is overcoming undesired spurious acoustic modes that can corrupt the filter response. These spurious modes vary, sometimes abruptly, with frequency and resonator dimensions. Current microresonator modeling techniques are insufficient to rapidly predict all the important spurious responses. Thus, in order to reliably design a filter, resonators at each new filter frequency must be fabricated and verified to be free of spurs before the filter can be realized using a second design, fabrication, and characterization cycle. A rapid (minutes) modeling technique to predict spurs is needed to reduce filter realization time and cost.

Fast and precise simulation methods are needed to predict the frequency response of microresonators and must include all higher order effects. However, due to their size and layer thicknesses compared to the wavelength, three-dimensional finite element models (3D-FEM) require many days of simulation time and only provide a snapshot of the overall response (e.g., impedance). To gain true physical insight, a fast simulation approach must capture diffraction, velocity dispersion and waveguiding simultaneously. Previously, we developed 1D coupling of modes (COM) models that predicted the 2D response of lamb waves in thin microresonator plates, reducing the simulation time from 15 minutes FEM to 1 second COM. Yet there remain additional effects to consider such as the contribution of reflection to waveguiding, where reflection decreases the velocity in the stopband causing the number of modes to differ from unperturbed propagation. To capture these effects have discretized the device in 2D and solved the COM equations across the complete structure using previously obtained COM coefficients. This is a new approach for microresonator design.

Summary of Accomplishments:

A 2D coupling of modes model has been developed to predict the spurious resonances in microresonators arising from acoustic wave interactions with the bus bar used to connected the interdigitated metal fingers that drive and sense the device. This model is also capable of rapidly modeling other lateral resonance affects such as reflections at the device anchors. The model predicts the close in spurs from the busing and reduces the simulation time needed to fully predict the device response from approximately 1 week to 30 minutes, allowing for optimization of the response.

Significance:

The ability to predict spurious modes in microresonators enables them to be deployed as filters in radios, radars and other radio-frequency communications systems vital for national security for both military applications important to DoD, and civilian applications important to DHS and DOE. The filters themselves make these electronic systems smaller, lower power, and more robust.

Temperature Dependence of the Electronic and Optoelectronic Properties of Carbon Nanotube Devices

162907

Year 1 of 2

Principal Investigator: F. Léonard

Project Purpose:

The detection of low levels of light in the infrared region of the electromagnetic spectrum is central to many applications across Sandia missions. Existing approaches for infrared detection use exotic semiconductor materials (e.g., HgCdTe), which raises issues with reliability, performance, and cost. This project is pursuing novel, potentially valuable approaches for optical detection that would use different materials, in particular ones compatible with existing complementary metal oxide semiconductor (CMOS) fabrication infrastructure. The advent of nanotechnology brings novel materials with unique properties for infrared detection; carbon nanotubes are particularly attractive, but much research and development is needed to establish firmly their electronic and optoelectronic properties.

Defect Localization, Characterization, and Acceleration Factor Assessment in Emerging Photovoltaic and Power Electronic Materials

164183

Year 1 of 3

Principal Investigator: B. B. Yang

Project Purpose:

Thin film photovoltaic (PV) materials systems, such as cadmium telluride (CdTe) and copper indium gallium selenide (CIGS), are promising approaches to producing affordable solar energy. Their reliability and degradation rate, however, still lag their traditional silicon counterparts. The success of alternative technologies, such as the microsystems-enabled photovoltaic (MEPV) technology, under development at Sandia, depends on good reliability and quantifiable longevity. The associated power conversion systems stand to benefit from the emergence of wide-bandgap materials systems, such as silicon carbide (SiC) and gallium nitride (GaN), but the long-term reliability of such devices is also untested and the failure mechanisms are not well understood.

The purpose of this project is to establish a failure analysis framework for these materials systems and examine the effects of accelerated testing in order to lay the groundwork for a physics-based, data-driven prognostics and health management (PHM) system applicable to specific degradation mechanisms.

The PV and the associated wide-bandgap power devices industry are relatively immature compared to their silicon-based microelectronics counterparts. As such, there is a weaker understanding of the physics behind performance degradation and device failure. This uncertainty makes the development of a PHM system with in situ monitoring inherently risky. The findings of the degradation mechanism may not relate to monitoring techniques that can be practically implemented. While microelectronics failure analysis concepts apply to these materials systems, they must adapt to different requirements, such as scale over resolution and foreign materials in the device and its packaging. Much of the investment risk lies in understanding the physics of failure and identifying a viable monitoring solution. This project, if successful, will eliminate much of the risk and lay out a clear path for efforts to developing a financially feasible approach to large-scale implementation of the PHM system.

Nano-Structured Silicon Phononic Crystals with Metal Inclusions for ZT Enhancement Proof-of-Concept

164672

Year 1 of 3

Principal Investigator: C. M. Reinke

Project Purpose:

Most published research on improvement of the thermoelectric figure of merit ($ZT = (S^2 \times \sigma / k)T$, where S , σ , and k are the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively, has largely focused on only one of its components, with the hope that the other two remain favorable. However, due to the interdependent nature of the problem, efforts to reduce k by incoherent phonon scattering inadvertently create electron scattering with a corresponding reduction in σ , and efforts to increase σ via doping typically decrease in S in accordance with the Mott relationship. We will attempt to circumvent these issues by addressing all three parameters of ZT simultaneously using nanostructured phononic crystals (PnCs). The engineered scattering of phonons using PnCs reduces k , while metal inclusions increase the σ of the PnC. Additionally, metallic nanoparticles will be implanted to engineer the electronic band structure at the semiconductor-metal interfaces in a manner that increases S , thus increasing the overall ZT .

Efforts to extend previous research in thermal conductivity reduction using PnCs to high-temperature, high- ZT devices raised questions about the constancy of the relative reduction in k at higher temperatures. Would σ be enhanced in a semiconductor-metal PnC (rather than semiconductor-air) while maintaining the reduction in k , and can S be enhanced using low-dimensional metallic inclusions? The first question will be answered by measuring the reduction in k relative to an unpatterned slab of the same thickness as the temperature is increased, and the second will be addressed by measuring the S , σ , and k of a Si-W PnC using an existing thermal equilibrium test bench. The third question will require careful introduction of metallic nanoparticles into the PnCs using focused-ion beams or ion implanter. All three tasks are supplemented by the theoretical expertise developed at Sandia in PnC design and thermal conductivity calculations for periodic nanoscale materials.

Gate-Controlled Diode Structure to Investigate Leakage Current and Early Breakdown in Graded InGaAsP/InP Junctions

164676

Year 1 of 3

Principal Investigator: D. Leonhardt

Project Purpose:

The purpose of the project is to understand the causes and mechanisms leading to the low breakdown voltage in phosphide-based semiconductor devices. Solutions to the early breakdown problem could enable the adoption of devices such as pnp heterojunction bipolar transistors for radiation-environment applications, leading to better device reliability compared to current technology. We have designed test structures to isolate surface versus bulk contributions to the early breakdown of the material. The test structures consist of diodes of varying area-to-perimeter ratios, differing geometries, and various crystallographic orientations. The test structures target surface effects that may contribute to early breakdown, while a series of different epitaxial structures will be used to characterize bulk material effects. Epitaxial structures will include homojunction InP diodes, heterojunction InGaAs/InP, graded layers, and quaternary InGaAsP diodes. The epitaxial structures will be used to investigate effects of built-in electric fields, interface states, material defects, and doping.

Alloys and Composites for Strong and Tough Freeform Nanomaterials 164677

Year 1 of 3

Principal Investigator: B. J. Kaehr

Project Purpose:

The pursuit of nanotechnologies has largely focused on the physics and chemistry of low-dimensional materials and their potential impact on areas such as electronics, catalysis, and medicine. However, a crucial class of materials remains largely unexplored at the smallest scales, namely alloys and composites that dominate modern manufacturing for mechanically robust (macroscopic) structures and devices. Of critical importance is the ability to manufacture “freeform” 3D designs and shapes using techniques such as casting.

Can engineered materials with freeform shapes be fabricated at nanoscales? Despite advances for developing nanomaterials with controlled composition, current synthetic practices generally limit forms to particles and wires. The development of nanoscale alloys with arbitrary form and controlled composition will require new material syntheses and manufacturing procedures.

This project is addressing this wholly unexplored area of materials science by adapting recent breakthroughs in 3D nanofabrication toward the synthesis of mechanically robust freeform alloys and composites. Specifically, we are focusing on 3D direct write methodologies for nanoscale materials comprised of alloys of iron (steels) and determine generalized strategies applicable to other alloy systems (e.g., Ti, Ni, Cu, Al). The challenges that arise for maintaining strength and toughness as features sizes approach minimum grain size, crack length, etc. will be mitigated via concurrent development of hierarchical freeform composites.

Recent advances in 3D printing have begun to usher in a new era for rapid prototyping. Considering available methodologies such as robocasting, stereolithography, and laser sintering, only multiphoton lithography (MPL) has the capability to fabricate feature sizes <100 nm. However, the range of materials compatible with this technique is currently very limited. This project will aim to substantially broaden this material space by building upon recent breakthroughs for MPL of metals and composites. Beyond advancing fundamental nanoscience, realizing nanoscale freeform alloys will facilitate design and fabrication of next-generation 3D device architectures.

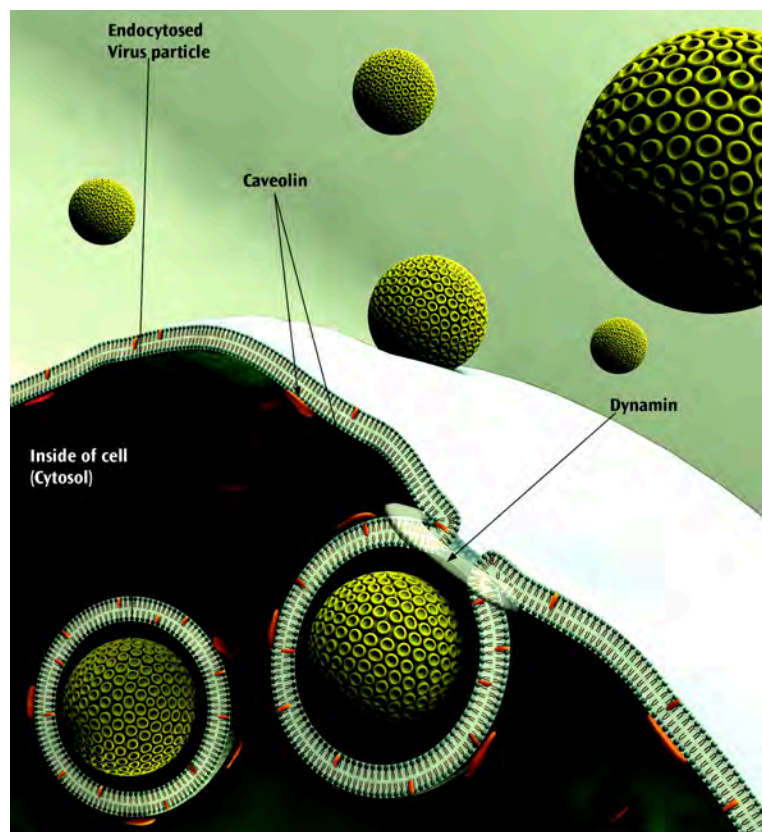
NEW DIRECTIONS INVESTMENT AREA

This investment area focuses on national security research fields into which Sandia has more recently embarked, and hence, tends to encompass initiatives that seek to draw existing Laboratory expertise into new applications for national security. Best exemplifying such initiatives are projects in biological sciences — with emphasis on alternative energy and biothreat reduction — projects at the nanotechnology-bioscience interface, and those in the cognitive sciences — particularly as applied to support for decision-makers.

Genome-Wide RNA Interference Analysis of Viral Encephalitis Pathogenesis Project 141530

This project is using siRNA (or RNAi—RNA interference) technology to inhibit the expression of genes that may be involved in viral infection, thereby determining what host-cell proteins are important in the infection processes by which biothreat/bioweapon viruses enter a cell (initial necessary step in infection), with the ultimate goal to develop methods to block infectivity.

Using genome-wide RNAi, 22,000 genes were screened for their potential role in the infection process of Rift Valley Fever Virus (RVFV) — a highly pathogenic virus that causes encephalitis (acute inflammation of the brain). The project showed that using RNAi to inhibit the process of caveolin-mediated endocytosis blocked viral entry, indicating that RVFV enters cells by caveolin-mediated endocytosis, rather than by clathrin-mediated endocytosis or micropinocytosis. This mechanism of entry was previously uncertain.



Artist's conceptual drawing of viral entry into a cell via caveolin-mediated endocytosis

From Sensing to Enhancing Brain Processes Project 141529

This project used electroencephalography (EEG) to study poorly understood brain waves that occur during memory consolidation. It is generally accepted that differences in neural activities resulting from contrasting remembered against not remembered items indicate neural activity during the time of memory encoding by the brain that is predictive of accurate recall or recognition (Dm). Generally, activity levels at encoding are higher for remembered items than for not remembered items.

The project characterized the Dm effect under different memory test conditions, recording so-called event-related potentials deriving from the activity of millions of neurons in the brain. Additionally it used two methodologies to attempt to intervene in — and improve — memory performance: cognitive training and transcranial direct current stimulation. Using human subject experiments and dynamical systems modeling the project assessed and attempted to augment the effectiveness of each of these interventions, testing their impact on both the Dm effect and on subsequent memory performance. The research discovered that strategic memory training — utilizing mental imagery to improve performance — improved the participants' performance across a wide range of memory tasks, while non-strategic working memory training impaired the participants' performance on some tasks. These findings indicate that adopting an appropriate memory strategy is likely to provide a bigger benefit to memory performance than interventions intended to increase memory capacity. Ultimately, the aim is to develop a paradigm that will establish causal links between recorded brain activity and task performance as well as to examine strategies that are appropriate to improve memory as compared with those that may be counterproductive.

Subject wearing a cap containing EEG electrodes for measurement of event-related brain potentials



New Directions Investment Area

Construction of an Abiotic Reverse-Electron Transfer System for Energy Production and Many Biocatalytic Pathways

141524

Year 3 of 3

Principal Investigator: E. Ackerman

Project Purpose:

All biomass energy is in high-density electron carriers, either organic (e.g., EtOH, butanol) or inorganic (e.g., H₂ or electricity). Converting biomass energy to fuels (concentrated electron carriers) is done in living communities via enzymes. Thermodynamic constraints to keep cells alive exert energy costs. Even a 'minimal cell' still has limited yields because it must sustain many unrelated reactions. Excess reducing equivalents are generated during metabolic reactions (e.g., bacteria channel two-thirds of their electron flow during glycolysis to make acetic acid rather than H₂, thus limiting yield). Current (unsuccessful) approaches that rely on engineering cells to overcome excess reducing equivalents cannot solve this bottleneck. This project has sought to harness components of known metabolons derived from multiple species to ultimately create an abiotic, or nonliving reactor via a reverse electron transfer (RET) system. Although many of the RET components will consist of proteins and cell-like and/or synthetic membranes, the core reaction centers will be enzyme based, albeit optimized for our streamlined reaction system, rather than to sustain living organism(s). This leading-edge work is difficult because: 1) not all components have been defined, even from living symbiotic systems surviving at the edge of what is thought to be thermodynamically possible and 2) considerable recombinant cloning and expression of "difficult" proteins will be required. (Difficult proteins are those requiring considerable effort to express in active form in milligram quantities.) Since this system will be freed from sustaining life to generate optimal energy yields, we have considerably more reaction design freedom, including unnatural amino acids, (electrically active) nanoporous materials, and artificial membranes. Successful pursuit of this research could have significant impact on approaches to economically feasible bio-inspired reactions. We are utilizing a high-throughput, cell-free protein expression system to make the relevant enzymes.

Summary of Accomplishments:

We analyzed the literature of syntrophic microbial systems to identify sets of relevant genes to create the reverse electron transport system. We then synthesized these genes, confirmed they were correct via second-generation DNA sequencing, then cloned them into relevant DNA and protein expression vectors, transcribed the DNA into mRNA, and then expressed multiple proteins using our wheat-germ cell-free expression system. We have also tested for enzyme activity using a variety of assays, all based on spectrophotometric absorption changes. To this end, we have utilized new 96-well plate readers from BioTek that are capable of reading samples in microtiter formats from 200 to 999 nm. We show that enzymes can be assayed directly from the cell-free translation reaction mixtures. However, the bottleneck in this work is trying to optimize the activity of the synthesized proteins. For example, we observe NADH + H⁺ + ubiquinone conversion to NAD⁺ and ubiquinol via one of our proteins. However, the only way to tell whether we have optimized activity is to try many different reaction conditions, such as varying salt (potassium vs. sodium), inclusion of cofactors, active-site metals, etc., again all at varying concentrations. An additional complication is that some enzymes work best when present in large, multi-enzyme complexes. Trying to optimize multiple conditions simultaneously for

multiple proteins is a time-consuming task. Our initial work has focused on making and verifying activities rather than optimizations. Once all of the proteins in a metabolic chain are made successfully, then we can try to connect them into an overall energy-generating system.

Significance:

This project vastly improved Sandia capabilities in molecular biology. The ability to make and study the “reagents of biological systems” is essential if Sandia is to have a serious impact on biology.

Aside from improving Sandia capabilities, the overall impact of this project is that we have hopefully generated sufficient data to impact the mission of DOE/BES (basic energy sciences) in terms of the possibility of transcending synthetic biology approaches toward efforts that are based on biology, but do not require living cells and, therefore, the overheads associated with keeping cells or communities of cells alive.

From Benchtop to Raceway: Spectroscopic Signatures of Dynamic Biological Processes in Algal Communities

141528

Year 3 of 3

Principal Investigator: J. A. Timlin

Project Purpose:

The purpose of this project is to: 1) discover spectroscopic signatures correlated to pond composition, photosynthetic efficiency, and lipid production at laboratory and pilot scales and 2) develop predictive computational models of algal growth and productivity at the industrial scale. Like lignocellulosic materials, there are major scientific challenges to an industrial-scale algal biofuels program. Recently, four broad areas of R&D needs have been identified for economically viable, industrial-scale cultivation of algae: 1) culture sustainability, 2) system productivity, 3) nutrient source scaling and sustainability, and 4) water conservation, management, and recycling. Progress in each of these areas is limited by significant knowledge gaps in fundamental algal biology. This project begins to address this shortcoming by applying a novel, multidisciplinary, multiscale approach utilizing Sandia's expertise in bioanalytical spectroscopy, chemical imaging, remote sensing, genomics, and computational modeling to investigate the effects that dynamic abiotic and biotic stressors have on algal photosynthesis, growth, and lipid production. Of particular note is the lack of research on the dynamic response to stressors encountered in the arid southwest ecosystem, a potential site of large-scale algal farms. The discoveries made on this project will produce fundamental knowledge of the underlying biological processes that govern algal growth and lipid production and thus enable gains in productivity and sustainability that are critical for optimizing cost-effective, industrial-scale algal facilities.

Summary of Accomplishments:

Over the lifetime of this project, we have developed Sandia's algal biology infrastructure to support a vibrant program in algal biofuels including the development of a fully staffed and stocked algal biology lab, support to key hires in bioenergy/biofuels, support to a total of five student interns in the field of biology and engineering, and development key collaborations with University of New Mexico and Arizona State University that have led to additional collaborative funding.

Major technical accomplishments over the lifetime of the project have included the following:

1. Development of remote, real-time detection of algal growth parameters at the benchtop and greenhouse scale, demonstration of technology at the raceway scale
2. Development of an improved and validated computational fluid dynamics model for algal growth in open channel raceways
3. Development of multidimensional and multiscale bioanalytics pipeline, application of this pipeline to understand CO₂ stress in production alga and salt stress in a model alga

Significance:

Our work fills a strategic niche in an important, yet largely unexplored area of biofuels where Sandia has unique capabilities. We have assembled a talented interdisciplinary team and are tackling critical challenges described in the National Algal Biofuels Roadmap. This creative technical approach has provided Sandia with differentiating bioanalytical capabilities in algal biology addressing cultivation at scale and is a critical step for future programs in algal biofuels research. Our research is directly relevant to the current national security mission of DOE's Energy Efficient and Renewable Energy, as

well as the current and future interests of DOE's Biological and Environmental Research and Advanced Research Projects Agency-Energy (ARPA-E) programs.

Refereed Communications:

T.A. Reichardt, A.M. Collins, O.F. Garcia, A.M. Ruffing, H.D.T. Jones, and J.A. Timlin,
"Spectroradiometric Monitoring of *N. Salina* Growth," to be published in *Algal Research*.

H.D.T. Jones, D.M. Haaland, M.B. Sinclair, D.K. Melgaard, A.M. Collins, and J.A. Timlin,
"Preprocessing Strategies to Improve MCR Analyses of Hyperspectral Images," to be published in the
Journal of Chemometrics and Intelligent Laboratory Systems.

From Sensing to Enhancing Brain Processes

141529

Year 3 of 3

Principal Investigator: L. E. Matzen

Project Purpose:

In this project, we aim to improve human performance by directly influencing brain activity. Our focus is on improving memory and decreasing memory errors for decision-relevant information. When people study information, their brains produce a signal that correlates with whether or not they will be able to remember that information later. This signal, called the Dm Effect, is not well understood, but it could potentially be used to predict future memory performance and thus to help people avoid errors. In this project, we are using electroencephalography (EEG) to characterize the Dm Effect under different memory test conditions. In FY 2012, we have extended our research on two intervention techniques that are hypothesized to improve memory performance: cognitive training and transcranial direct current stimulation (tDCS). We are using human subject experiments and dynamical systems modeling to assess and augment the effectiveness of each of these interventions. We are testing their impact on both the Dm Effect and on subsequent memory performance, a paradigm that will establish causal links between recorded brain activity and task performance.

This project is creating a framework for using brain activity to create focused interventions that improve human performance. We will combine cognitive training and tDCS techniques in new, targeted ways, and use EEG and computational modeling to assess their ability to optimize brain activity for specific individuals and tasks. This multifaceted approach will produce novel experimental evidence regarding the relationship between brain activity and memory performance. This information will be direct evidence that cannot be obtained from traditional correlational studies, and would represent a significant advance in the science and application of cognitive neuroscience. In addition, if the techniques employed in this project, alone or in combination, can produce substantial enhancements in memory performance, they can be applied to improving performance in individuals whose jobs involve high-consequence decision making.

Summary of Accomplishments:

We demonstrated for the first time that brain activity recorded while a person studies information can be used to predict how well that person will perform on a subsequent memory test. This novel finding used a computational model of event-related potentials (ERPs) to classify people based on how closely their brain activity at study matched an “optimal” approach to memorizing the to-be-learned information. The model successfully predicted which learners would perform best when they were tested on their memory for the studied information.

In addition to predicting future memory performance based on brain activity, we investigated the effects of cognitive training on both brain activity and behavioral memory performance. Three groups of participants completed a cognitive training study in which one group received no cognitive training (control group), one group received training on how to use a mental imagery strategy to improve their memory performance (strategic memory training), and one group received working memory training designed to increase their working memory capacity (non-strategic memory training). We discovered that the strategic memory training improved the participants’ performance across a wide range of memory tasks, while the non-strategic working memory training actually impaired the participants’

performance on some tasks. These findings indicate that adopting an appropriate memory strategy is likely to provide a bigger benefit to memory performance than interventions intended to increase memory capacity.

Significance:

This project was the first to attempt to use ERPs to predict a person's future performance. We successfully demonstrated that ERPs can be a useful predictive tool and replicated this finding across several different experiments and participant populations. This finding has numerous applications for improving human performance. For example, these findings lay the framework for developing augmented learning systems that could alert a learner to cases where he or she is likely to forget the studied information. In addition, the results of the cognitive training study emphasize the importance of training people to use appropriate learning strategies.

Refereed Communications:

A.S. Benjamin, M. Diaz, L.E. Matzen, and B. Johnson, "Tests of the DRYAD Theory of the Age-Related Deficit in Memory for Context: Not about Context, and not about Aging," *Psychology and Aging*, vol. 27, pp. 418-428, June 2012.

Genome-Wide RNA Interference Analysis of Viral Encephalitis Pathogenesis 141530

Year 3 of 3

Principal Investigator: O. Negrete

Project Purpose:

The highly pathogenic viruses that cause encephalitis (acute inflammation of the brain) include a significant number of emerging or re-emerging viruses that are also considered potential bioweapons. Rift Valley Fever virus (RVFV) is a prime example of such a virus that causes serious morbidity and mortality in both humans and livestock. The lack of efficient countermeasure strategies, the potential for dispersion into new regions, and the pathogenesis in humans and livestock make RVFV a serious public health concern. RVFV infects a broad host range indicating that the host requirements for virus entry and replication are widely distributed. To date, a systematic analysis of the host factors involved in RVFV infection and pathogenesis have not been described. To identify host proteins that are required for RVFV infection, we used RNA interference (RNAi) technology, a powerful genomic approach used to investigate host factors involved in virus replication on a systems level. Additionally, to improve the efficiency and speed of genomic screening in high-level biocontainment, we developed a miniaturized microfluidic platform to perform RNAi screening.

Summary of Accomplishments:

During the course of this project we achieved, three major milestones.

1. First, we conducted a genome-wide RNAi screen to identify host factors involved in RVFV infection. The RNAi screen individually evaluated the role of 22,000 human genes in RVFV cell entry and replication. The primary screen identified 2556 hits. These genes were reevaluated in a secondary screen and the role of 473 cellular genes whose knockdown reduced viral infection by 34% or more in 5 independent plates was confirmed. These genes were classified into 30 different canonical pathways including endocytosis, signaling G protein coupled signaling to phospholipase C, locomotion, chemotaxis, and cell matrix adhesion.
2. We met our second milestone when we followed up on a novel endocytosis pathway used by Rift Valley Fever virus for cell entry. Using cellular perturbations that include chemical inhibitors, RNAi, and overexpression of dominant negative proteins, while controlling for nonspecific effect of these inhibitor using two other viruses known to enter cells by macropinocytosis or clathrin coated pits, we found that RVFV enters cells through caveolae-mediated endocytosis.
3. Our final milestone was achieved when we developed a miniaturized high-throughput microfluidic RNAi screening platform. The microfluidic device design is based on cellular microarray technology, created on microscope slides that use chemical means to introduce small interfering RNA (siRNA) in mammalian cells. Polydimethylsiloxane (PDMS)-based microchambers and channels enclose the siRNA spots thus minimizing reagent consumption, numbers of cells used per experiment and preventing contamination issues observed in open systems. Two viruses, including emerging infectious disease model RVFV, were used to validate the RNAi screening platform specifically intended to identify viral endocytosis pathways, thereby providing valuable insight into host-pathogen interactions. The techniques for miniaturized RNAi screening are adaptable to other well-characterized infection pathways with a potential for large-scale screening required for genome-wide analysis.

Significance:

RVFV is on the national biodefense priority pathogens list as a category A agent and identifying new therapeutic targets to combat RVFV infection is of national security interest to numerous federal agencies such as DHS. Our results provide an understanding of the mechanisms used by RVFV to invade cells and cause infection, and this understanding can lead to development of therapeutics that target virus entry. Also, by building microscale devices to transport into BSL3 labs in need of small-footprint equipment, we can improve the speed at which these discoveries are made for pathogens of high disease consequence.

Refereed Communications:

B. Harmon, B.R. Schudel, D. Maar, C. Kozina, T. Ikegami, C.-T.K. Tseng, and O.A. Negrete, “Rift Valley Fever Virus Strain MP-12 Enters Mammalian Host Cells via Caveolae-Mediated Endocytosis,” to be published in the *Journal of Virology*.

Neurological Simulations for Emerging Brain Maps 141531

Year 3 of 3

Principal Investigator: R. Schiek

Project Purpose:

Advances in imaging and reconstruction technologies are driving many research projects to map all of the neurons in some small animal brains. While these projects will produce detailed topology of their targeted subjects, the ability to then simulate in detail the neurophysiology is limited to high-fidelity simulations of a few neurons, or lower-fidelity simulations of thousands of neurons. Sandia's parallel circuit simulator, Xyce, can address large-scale neuron simulations in a new way by greatly extending the range within which one can perform high-fidelity, multi-compartment neuron simulations. This enables new science in understanding how collections of neurons produce macroscopic behavior.

Additionally, the network simulation framework provided by Xyce can be used to migrate high-level, cognitive models to a high-performance computing platform and couple such models to lower-level neuron based systems. To be successful, this work must engage the neuroscience community and researchers developing the brain maps by providing access to Xyce and demonstrating that Xyce can tackle complex problems. Since the topology of a neural system is more highly linked than a circuit, improved preconditioning and new solver technologies may also be needed as well as new computational tools (i.e., reduced-order modeling). Programmatically, this project will connect the cognitive science work at Sandia to the high-performance computing community and provide context for further engagement between Sandia and the neuroscience simulation community.

Summary of Accomplishments:

A key challenge to this work from its start was to address multiple levels of abstraction in neuron modeling within this one simulation framework. While the analogy and connection between fine-scale, compartmental neuron modeling and electrical simulation is straightforward, it was less obvious how to efficiently work at higher levels of abstraction. We have identified and implemented population-level models that can be used in studies of neurogenesis and plasticity in learning and memory. This population modeling is significant for two reasons. First, it can still couple to detailed neuron models allowing one to study systems at multiple levels of fidelity. Second, the population level model allows for rapid changes in neuron number and connectivity, which are system level changes that are difficult fit within the sparse matrix structure of a network, ordinary differential equation solver.

A second key development this year is the scaling studies of neuron systems with high levels of synaptic connectivity. Anatomical studies have found that a single neuron may be connected to other neurons by thousands or tens of thousands of synapses. This high level of connectivity could pose significant problems in the parallel partitioning and preconditioning of the problem for simulation. We have studied systems with 200 synapses per neuron and have found good scaling up to 64 processors.

Finally, this work culminated in the application for a National Institutes of Health grant to continue this research and extend it to the analysis of neurological system dynamics.

Significance:

This work demonstrates how modern techniques in parallel computing can benefit computational neuroscience. Significant in this work is how the parallel implementation of the simulation is separated from the description of the problem (i.e., the researcher does not have to change the problem to fit it into a parallel framework). This enables domain experts in one field (parallel solvers) to directly accelerate the work of computational neuroscience. This aligns well with the DOE theme of scientific discovery and innovation.

Real-Time Neuronal Current Imaging of the Human Brain to Improve Understanding of Decision-Making Processes

141532

Year 3 of 3

Principal Investigator: H. D. Jones

Project Purpose:

Understanding the cognitive processes that underlie decision making will enable Sandia to determine variables that positively and negatively impact the ability to make optimal decisions under stress and uncertainty — situations regularly encountered in national security domains. A major limitation in understanding the neuronal basis of decision making is the lack of imaging technologies capable of directly measuring the neuronal response to cognitive challenges with high temporal and spatial resolution. Magnetoencephalography (MEG) and electroencephalography (EEG) have impressive temporal resolution (millisecond), but are limited in their ability to localize the neuronal signal, especially for deep sources. In contrast, functional magnetic resonance imaging (fMRI) has high spatial resolution (millimeter), but poor temporal resolution due to its dependence on the temporally sluggish vascular response. The proposed project will develop complementary technologies (fMRI and proton magnetic resonance spectroscopy [¹HMRS]) to directly detect neuronal responses during perceptual decision making by investigating the effects of synchronously firing cortical neurons (and their associated magnetic fields) on the water proton signal. These event-related magnetic fields (ERFs) are putatively the same fields that would be detected by MEG. However, by detecting them with a magnetic resonance (MR)-based method, the sources of the fields can be precisely located and a true neuronal current (NC) imaging method can be devised. The NC effect on the ¹HMRS signal is expected to be weak and hampered by scanner and physiologic noise. Therefore, Sandia's demonstrated area of expertise in signal processing and multivariate data analysis of spectral image data including Sandia's patented Multivariate Curve Resolution (MCR) methods will be applied to the ¹HMRS data to improve the sensitivity to small neuronal responses during decision-making events. This novel approach is intended to provide brain researchers with a new and powerful functional brain imaging capability that will have unprecedented spatial and temporal resolution and can ultimately be used to improve our understanding of decision making.

Summary of Accomplishments:

The task of searching for the neuronal current (NC) signal in magnetic resonance data was embarked upon as a high-risk, high-payoff project. Numerous studies in the past have failed to find evidence of neuronal currents when using magnetic resonance imaging applied to normal human subjects with various stimuli presented. We chose to take a fundamentally different approach than has been used in the past. Instead of using Magnetic Resonance Imaging approaches, we chose to examine the subtle changes in the Free Induction Decay (FID) data from Proton Magnetic Resonance Spectroscopy caused by the presence of stimulus induced neuronal currents in subjects using a single fixed voxel. Our previous experience with statistical approaches and Multivariate Curve Resolution methods applied to various spectral data gave us the tools to detect, discover, and identify extremely small changes in the data due to perturbations. Our initial human subject experiments examining a single voxel in the visual cortex during visual stimulation in the absence of the hemodynamic Blood Oxygen Level Dependent (BOLD) response yielded statistically significant differences between the FIDs with the NC present and those FIDs where it was absent. The changes in the shape of the FIDs were consistent with changes expected from NC, but other causes for the differences, such as a startle response, could not be ruled out in these data. Two subsequent experiments, with BOLD present and BOLD absent, used auditory stimulation as a control to eliminate startle as the cause of the mild significant differences in the first

experiment. Unfortunately, neither of studies was able to replicate our initial positive result. Even if the results from the first experiment were evidence of NC detection, it is clear that its effect is so small that a true NC imaging experiment would not be possible with conventional MR instrumentation.

Significance:

A magnetic resonance system capable of directly imaging neuronal current distribution would be of great utility to neuroscience and medicine by allowing researchers or clinicians to map neuronal dynamics associated with a given stimulus at both high spatial and temporal resolution in the brain. In addition to aligning with the DOE theme of scientific discovery and innovation, the ability to map neuronal dynamics could, in the future, be of interest to DoD and other federal agencies wishing to more readily predict performance criteria. Electroencephalography and magnetoencephalography measure the electromagnetic fields to estimate the location and size of an equivalent current dipole in the brain by inverse modeling and have high temporal resolution but poor spatial resolution. Functional magnetic resonance imaging is based upon an indirect hemodynamic response, which provides a high- resolution image but has poor temporal resolution.

Nature Versus Nurture in Cellular Behavior and Disease

141704

Year 3 of 3

Principal Investigator: C. J. Brinker

Project Purpose:

There is now overwhelming evidence of environmental influences on cellular behavior. For example, many drugs screened/developed against 2D cell cultures in vitro are often ineffective against the same cells contained within 3D environments in vivo. Environmental effects are crucial to understanding a diverse spectrum of problems including cancer metastasis, drug resistance, tuberculosis dormancy, and nanoparticle toxicology. For example, it is proposed that cancer cells may use a quorum sensing mechanism similar to bacteria to regulate multicellular functions and control steps in metastatic colonization. Progress in addressing these problems is currently hindered by: 1) an inability to incorporate cells into 3D architectures that better represent the nanostructured, 3D extracellular matrix (ECM), tissues, or niches, where cells may reside in vivo and 2) an inability to selectively target and deliver effective therapeutics to dormant/drug resistant cell populations.

This project is pursuing two complementary, interrelated goals: 1) the incorporation of individual or groups of bacterial, fungal, or mammalian cells within novel 3D cell-built or lithographically defined matrices that provide an engineered chemical and physical background to inform cells and direct their behavior and 2) the development of two classes of targeted nanoparticle delivery platforms, protocells (porous nanoparticle supported lipid bilayers) and virus-like particles (VLPs), which could be selected against arbitrary dormant/drug resistant/metastatic cells and selectively deliver multicomponent cargos (cocktails) to this recalcitrant population. This project provides a unique means to understand environmental influences on cellular behavior, in particular, dormancy, drug resistance, metastasis and nanoparticle toxicology. It will enable the development of new targeting and drug delivery strategies designed to selectively attack and kill dormant and drug resistant cells, thereby reducing a significant reservoir of human disease. It will establish the scientific basis for creating new classes of cell based sensors, and it will provide a platform with which to understand nanoparticle toxicology in 3D environments, which better represent in vivo conditions.

Summary of Accomplishments:

1. We adapted cell-directed dormancy to the 3D integration of cancer cells. Integrated cells are nonreplicative and drug resistant but maintain biofunctions like protein production, pinocytosis and receptor mediated endocytosis. These dormant cell states are resistant to external threats and could serve as reporters of environmental/battlefield conditions or as autonomous factories for enzyme production. Inducing cancer dormancy would be a breakthrough cancer therapy.
2. Using multiphoton protein lithography, we fabricated arbitrary 3D biomolecular architectures with retained biomolecular activity and optically defined modulus and deposition of nanomaterials. Such structures serve as scaffolds in which to display enzymes and catalysts to achieve coupled spatially defined chemical reactions. They also serve as micro-environmental chambers in which to study and direct cellular behavior.
3. We discovered a generalized process, Silica Cell Replication, wherein mammalian cells direct their exact replication in silico. The silica cell replicas preserve nm- to macro-scale cellular features and dimensions after complete drying. Upon re-exposure to water, preliminary experiments show retention of enzymatic activity without refrigerated storage.

4. We invented a targeted, versatile nanoparticle-based drug delivery platform called the protocell. Targeted protocells (cover articles in *Nature Materials*, *ACS Nano*, and *Advanced Health Care Materials*) are formed by fusion of lipid bilayer membranes on high-surface-area porous silica nanoparticle cores followed by conjugation with a targeting ligand. We showed that the combined stability, cargo capacity, and targeting selectivity of protocells result in a million-fold improvement in selective cytotoxicity to cancer compared to the corresponding Food and Drug Administration (FDA)-approved liposomal delivery agent.
5. We demonstrated selective delivery of nanoparticles, chemotherapeutic drugs, siRNA cocktails, and protein toxins to cancer with protocells and MS2 virus-like particles (3 cover articles in *Nature Materials* and *ACS Nano*). The delivery efficiency was documented to exceed by orders of magnitude that of alternative nanocarriers.

Significance:

This project contributed substantially to Sandia's DOE nanoscience, DHS, and national security missions. Cellular integration within engineered 3D matrices has created new biotic/abiotic functional nanocomposites that could serve as ultrasensitive cell-based environmental sensors (DHS/national security [NS]/DTRA) or platforms for studying/directing behavior at the individual cell level, relevant to immune response and outbreak of disease (DHS/NS). Protocells and VLPs represent two breakthrough multifunctional nanoparticle systems important for drug delivery, imaging, and ultrasensitive sensors of arbitrary targets (DHS/NS).

Refereed Communications:

H. Zhang, D.R. Dunphy, X. Jiang, H. Meng, B. Sun, D. Tarn, M. Xue, X. Wang, S. Lin, Z. Ji, R. Li, F.L.; Garcia Jr., J. Yang, M.L. Kirk, T. Xia, J.I. Zink, A. Nel, and C.J. Brinker, "Processing Pathway Dependence of Amorphous Silica Nanoparticle Toxicity: Colloidal vs. Pyrolytic," *Journal of the American Chemical Society*, vol. 134, pp. 15790-15804, August 2012.

E.C. Dengler, A. Kerwin, J. Liu, C.M. Olcott, B.N. Bowman, L. Armijo, K. Gentry, J. Wilkerson, J. Wallace, C.J. Brinker, and E.D. Milligan, "Mesoporous Silica-Supported Lipid Bilayers (Protocells) for DNA Cargo Delivery to the Spinal Cord," to be published in the *Journal of Controlled Release*.

K. Epler, D. Padilla, G. Phillips, P. Crowder, R. Castillo, D. Wilkinson, B. Wilkinson, C. Burgard, R. Kalinich, J. Townson, B. Chackerian, C. Willman, D. Peabody, W. Wharton, C.J. Brinker, C. Ashley, and E. Carnes, "Targeted Delivery of Protein Toxins: Delivery of Ricin Toxin A-Chain by Peptide-Targeted Mesoporous Silica Nanoparticle-Supported Lipid Bilayers," *Advanced Healthcare Materials*, vol. 1, p. 241, May 2012.

J.C. Harper, T.L. Edwards, T. Savage, S. Harbaugh, N. Kelley-Loughnane, O. Stone, C.J. Brinker, and S.M. Brozik, "Orthogonal Cell-Based Biosensing: Fluorescent, Electrochemical, and Colorimetric Detection with Silica-Immobilized Cellular Communities Integrated with an ITO-Glass/Plastic Laminate Cartridge," *Small*, vol. 8, p. 2613, September 2012.

C.E. Ashley, E.C. Carnes, K.E. Epler, D.P. Padilla, G.K. Phillips, R.E. Castillo, D.C. Wilkinson, B.S. Wilkinson, C.A. Burgard, R.M. Kalinich, J.L. Townson, B. Chackerian, C.L. Willman, D.S. Peabody, W. Wharton, and C.J. Brinker, "Delivery of Small Interfering RNA by Peptide-Targeted Mesoporous Silica Nanoparticle-Supported Lipid Bilayers," *ACS Nano*, vol. 6, pp. 2174-2188, February 2012.

L.D. Zarzar, P. Kim, M. Kolle, C.J. Brinker, J. Aizenberg, and B. Kaehr, "Direct Writing and Actuation of Three-Dimensionally Patterned Hydrogel Pads on Micropillar Supports," *Angewandte Chemie International Edition*, vol. 50, pp. 9356-9360, September 2011.

Genetic Engineering of Cyanobacteria as Biodiesel Feedstock

142441

Year 3 of 4[†]

Principal Investigator: A. Ruffing

Project Purpose:

The purpose of the project is to genetically engineer cyanobacteria for the production of hydrocarbons to be used for biodiesel feedstock. While most efforts in biofuel production from photosynthetic microorganisms focus on the natural oil-producing eukaryotic algae, this project investigates the use of fast-growing, prokaryotic, photosynthetic organisms with established methods of genetic engineering. Moreover, cyanobacteria have been shown to naturally secrete hydrocarbons such as free fatty acids, simplifying the downstream collection and purification of the biodiesel feedstock. This is advantageous compared to the intracellular accumulation of triacylglyceride (lipid) in eukaryotic algae, which can be difficult to extract.

Two model cyanobacteria, *Synechococcus elongatus* PCC 7942 and *Synechococcus sp.* PCC 7002, are engineered for the production of free-fatty acids (FFA), a potential biodiesel feedstock. For FFA production, the engineering strategy includes four main steps: 1) elimination of FFA metabolism, 2) removal of feedback inhibition of the fatty acid (FA) biosynthesis pathway, 3) improving carbon flux through the FA biosynthesis pathway, and 4) enhancing carbon fixation. The engineering strategy utilizes novel genes cloned from the green alga, *Chlamydomonas reinhardtii*. As *C. reinhardtii* is a natural oil producer, the FA biosynthesis enzymes from this organism may have greater activity than the *Synechococcus* native enzymes. Genetic engineering of the natural FA pathway may lead to changes in the cell and photosynthetic membranes. Several techniques are used to characterize changes in membrane composition and photosynthesis, including electrospray ionization-mass spectroscopy (ESI-MS), confocal hyperspectral fluorescence imaging, and pulse-amplitude-modulated (PAM) photosynthesis yield analysis. Changes at the genetic level are analyzed using RNA-seq, a sequence-based technology for analysis of gene expression levels.

The PI is a President Harry S. Truman Fellow.

[†] This 36-month project spans four fiscal years

Diffusion among Cognitively Complex Agents in Limited Resource Settings 148898

Year 3 of 3

Principal Investigator: K. Lakkaraju

Project Purpose:

The S&T objective of this work is to study diffusion of information in complex settings, i.e., ones that exhibit: 1) socially complex agents (differing numbers of neighbors, captured through a social network); 2) cognitively complex agents (continuous, interdependent belief structures that change over time, rather than binary, independent belief structure, captured through a cognitive network); and 3) limited resources (bounded rationality, modeled by limiting the resources for communicating and integrating information). Current diffusion models focus on social structure, leaving cognitive structure simple. We propose to develop a novel model of diffusion that exhibits these three factors.

This is a high-risk project because, to our knowledge, no one else has developed a model with complex cognitive agents. The hypothesis of this project is that diffusion will increase in speed as a function of an increase in the connectivity of the social network and a decrease in the connectivity of the cognitive networks of individual agents. We are testing this hypothesis by developing a model of diffusion, implementing the model in a simulation framework, and then measuring the speed of diffusion (number of interactions) as we vary the connectivity of the cognitive and social networks. The intention of this project is to develop a model that will allow one to ask basic research questions about the interaction between cognitive networks and social network structure.

Summary of Accomplishments:

- We developed a model of attitude change incorporating positive/negative information: it captures bidirectional reasoning where conclusion impacts evidence assessment.
- We evaluated the attitude change model and established its dynamics as being similar to known attitude change results.
- We evaluated the impact of cognitive effort on attitude change.
- We investigated the impact of community-structured graphs on attitude change.
- We designed an experiment to gather data for calibration/validation using Amazon Mechanical Turk™. Preliminary survey results were gathered.
- We provided expertise to DOE HQ Institutional Review Board (IRB) on de-identification for data sharing.

Significance:

Understanding the factors that influence the speed of diffusion is important in numerous areas: DOE (diffusion of climate change information), DoD (the spread of tactics, techniques, and procedures [TTPs]), and DHS (developing communication strategies to quickly spread safety-critical information to enhance community resiliency in the face of disasters or sustained threats such as improvised explosive device [IED] campaigns). DOE will benefit as we can model the diffusion of climate change information; in addition the diffusion of TTPs (such as IED tactics) is important for helping DoD understand capability evolution between theatres of operation. DHS will benefit from understanding the diffusion of critical safety information that could impact the resiliency of a community.

Refereed Communications:

K. Lakkaraju, S. Swarup, and L. Gasser, “Consensus under Constraints: Modeling the Great English Vowel Shift,” in *Proceedings of the 2012 Social-Computing, Behavioral-Cultural Modeling, and Prediction Conference*, pp. 1-8, 2012.

C.M. Vineyard, K. Lakkaraju, J. Collard, and S. J. Verzi, “The Impact of Attitude Resolve on Population Wide Attitude Change,” in *Proceedings of the 2012 Social-Computing, Behavioral-Cultural Modeling, and Prediction Conference*, pp. 322-330, 2012.

K. Lakkaraju and A. Speed, “A Cognitive-Consistency Based Model of Population Wide Attitude Change,” in *Proceedings of Complex Adaptive Systems: Views from the Physical, Natural, and Social Sciences*, 2012.

K. Lakkaraju and A. Speed, “Population Wide Attitude Diffusion in Community Structured Graphs,” in *Proceedings of the 2011 AAAI Fall Symposium on Complex Adaptive Systems*, 2011.

Ultrasensitive, Amplification-Free Assays for Detecting Pathogens

149705

Year 3 of 3

Principal Investigator: R. Meagher

Project Purpose:

Quantitative analysis of nucleic acids (DNA or RNA) is a powerful approach for detecting and identifying pathogens, including potential bioweapons and pandemic threats. All current approaches for nucleic acid detection short of direct sequencing (e.g., microarrays, polymerase chain reaction [PCR], blots) rely upon hybridization of nucleic acid primers or probes to a specific target sequence. Most assay formats require enzymatic amplification like PCR to generate a high enough concentration of nucleic acid for detection. PCR-based methodologies are sensitive and powerful, but require a well-equipped lab, with cold storage and clean samples — enzymatic approaches are sensitive to contaminants and inhibitors in environmental samples.

Rather than using PCR to generate 10^8 or more copies of a template in a ~ 100 μL reaction volume, we are working to confine the total nucleic acid content of a sample into a volume of ~ 100 pL adjacent to a nanoporous polymer membrane (roughly 10^6 -fold increase in concentration). The total contents of the concentrated sample volume can be directly analyzed by microchannel electrophoresis, with minimal dilution of the sample plug. A simple detector with ~ 100 pM sensitivity could thus detect hybridization of $\sim 6,000$ target molecules, which corresponds roughly to the number of ribosomal RNA molecules in a single bacterial cell.

We are pursuing a proof-of-concept study, including experimental demonstrations of the assay with model bacterial and viral targets, coupled with analytical and computational modeling of the underlying transport and kinetic processes. Transport modeling will provide an estimate of the maximum rate of nucleic acid concentration, and concentration profiles of multiple ionic species involved in hybridization, which will be used to develop a kinetic model for hybridization. The resulting theoretical estimates of assay performance will be used to benchmark our experimental investigations, enabling us to optimize parameters such as membrane chemistry, buffer systems, electric field, and temperature cycling.

Summary of Accomplishments:

Hybridization of nucleic acid probes has the potential to directly detect pathogens without requiring resource-intensive amplification steps, but conventional approaches to direct hybridization are typically slow or suffer from low sensitivity. In this work, we have characterized a novel approach for rapid detection of low-abundance nucleic acids by direct hybridization in solution, with sensitive analysis enabled by electrophoretic preconcentration of nucleic acids at a nanoporous membrane. We performed proof-of-concept testing of the assay using a model DNA virus, showing direct detection of as little as 400 amol (atto moles) (~ 240 million copies) with current (un-optimized) hardware. One to two orders of magnitude lower detection limits can be expected with modest improvements to the device. For clinical detection of low-abundance pathogens, the assay needs to be coupled to an extraction technique for concentration of nucleic acid from large volume samples.

We extensively characterized the membrane preconcentration process for DNA, and determined rates of preconcentration and efficiency of recovery as a function of preconcentration conditions, membrane formulation, and DNA size. A key result of this testing is that, in most circumstances, an uncharged

membrane outperforms a negatively charged membrane, in terms of the rate of preconcentration, stability of operation, and quality of the subsequent separation. Theoretical analysis suggests minimal time is saved by performing hybridization on the device at the membrane, as opposed to off the device. Meanwhile, performing the hybridization off-chip allows easier control over hybridization conditions. The membrane preconcentration device also enables rapid, ultrasensitive size-based separation of nucleic acids, and has been demonstrated for multiplex PCR analysis of drug resistance genes in bacteria. For size-based separations of DNA, the membrane preconcentration chip offers ~100-fold better sensitivity than the commercial Agilent Bioanalyzer, and an order of magnitude faster results than capillary electrophoresis.

Significance:

The hybridization assay can be coupled to portable nucleic acid extraction hardware currently under development for rapid, amplification-free detection of DNA and RNA signatures from pathogens. The membrane preconcentration process itself is a powerful technology that greatly extends the sensitivity of size-based separations of nucleic acids, particularly when rapid results or portable operation is necessary. Theoretical analysis provides insight into the electrokinetic phenomena at work during membrane preconcentration, and provides guidance into optimal strategies for utilizing membrane preconcentration. In addition to aligning with the DOE theme of scientific discovery and innovation, the ability to detect nucleic acids with enhanced sensitivity is of potential interest to DHS and other federal agencies concerned with homeland security and the defeat of bioterrorism.

Refereed Communications:

R.J. Meagher and N. Thaitrong, "Microchip Electrophoresis of DNA following Preconcentration at Photopatterned Gel Membranes," *Electrophoresis*, vol. 33, pp. 1236-1246, April 2012.

An Adaptive Approach to Modeling Human Reasoning

150966

Year 3 of 3

Principal Investigator: D. J. Stracuzzi

Project Purpose:

Inference techniques play a central role in many cognitive systems. They transform low-level observations of the environment into high-level, actionable knowledge that then gets used by mechanisms that drive action, problem solving, and learning. This work makes an initial effort at combining results from artificial intelligence (AI) and psychology into a pragmatic and scalable computational reasoning system. Our approach combines a numeric notion of plausibility with first-order logic to produce an incremental inference engine that is guided by heuristics derived from the psychological literature.

This research is exploring a combination of computational reasoning techniques needed to emulate the powerful and pragmatic nature of human reasoning. This distinguishes the proposed work from past efforts at computational reasoning, which tend to focus on a single technique and ignore the question of how to decide which method to use in a given situation. The project is addressing questions about how to represent knowledge, combine computational reasoning techniques, and incorporate the effects of learning and experience on reasoning in psychologically plausible ways. A key goal is to identify a psychologically plausible computational mechanism for guiding the reasoning process.

If successful, this work will provide a foundation for future research on human decision making, automatic knowledge base acquisition, fusion of low-level state descriptions into high-level, actionable knowledge, and neurally plausible models of high-level reasoning mechanisms, all of which are likely to play critical roles in future research.

Summary of Accomplishments:

Scientific and technical achievements include development of a mathematical framework for combined logical and statistical reasoning, along with incorporation of several well-known psychological biases. Key lessons learned surround the development of the underlying knowledge representation, which now supports both the computational and psychological aspects of the system quite naturally. Specifically, we discovered a graph-like representation that emulates many useful properties of hypothesized psychological structures. Other accomplishments include a smooth integration of logical and statistical information into the system such that the algorithms required for processing the information execute in an online manner and require minimal computation. With respect to applications, we identified several mission-relevant opportunities to which the results of this work are relevant. Specific tasks include aerial and satellite image analysis, cyber intrusion detection, and as the basis for realistic intelligent entities in training simulations. To date, work from the project has been accepted to two conferences, one in the form of a paper and poster presentation, the other in the form of an oral presentation.

Significance:

The integrated approach to reasoning and learning taken by this project has clear implications for applied research in both the DOE mission in cyber security and DoD's needs in aerial image processing. Both of these mission-relevant areas suffer from the same problem: the volume of data streaming in from sensors (information networks and satellite images) is quickly outpacing the processing capabilities of human analysts. Our approach provides the foundation for computational systems that combine low processing costs with a unique ability to distinguish between anomalous and malicious activity. These will be critical aspects of any system that deals with "big data" issues.

Tailoring Next-Generation Biofuels and their Combustion in Next-Generation Engines

151308

Year 2 of 3

Principal Investigator: C. A. Taatjes

Project Purpose:

Increasing energy costs, the dependence on foreign oil supplies, and environmental concerns have emphasized the need to produce sustainable renewable fuels and chemicals. Domestically produced biofuels for the transportation sector will be key to meeting national goals for energy security and climate-change mitigation. The strategy for producing next-generation biofuels must include efficient processes for biomass conversion to liquid fuels and the fuels must be compatible with current and future engines. New clean and efficient combustion strategies that rely on compression ignition are extremely sensitive to changes in fuel chemistry. Nevertheless, biofuel development generally takes place without any consideration of combustion characteristics, and combustion scientists typically measure biofuels properties without any feedback to the production design. We seek to optimize the fuel/engine system by bringing combustion performance, specifically for advanced next-generation engines, into the development of novel biosynthetic fuel pathways.

We propose an innovative coupling of combustion chemistry, from fundamentals to engine measurements, to the optimization of fuel production using metabolic engineering. We will develop and engineer a new platform for drop-in fuel production from lignocellulosic biomass, using endophytic fungi, and concurrently generate and exploit a combustion chemistry knowledge base to tailor the biosynthesis. Current biofuels production from lignocellulosic material starts with pretreatment and enzymatic hydrolysis to obtain monomeric sugars, which are then fermented. Our new biosynthetic approach will avoid these two costly steps, by using a consolidated process that directly breaks down lignocellulosic biomass by extracellular hydrolytic enzymes and produces an infrastructure-compatible biofuel by fermenting the liberated monomeric sugars. We will investigate the fuel's performance in clean high-efficiency advanced engines and construct predictive combustion chemistry models to guide the optimization towards high-performance compounds. This project will establish, for the first time, the necessary connections among the fundamental chemistry, engine science, and synthetic biology for fuel production, building a powerful framework for the co-development of engines and biofuels.

From Neurons to Algorithms

151345

Year 2 of 3

Principal Investigator: F. Rothganger

Project Purpose:

How does the human mind work? This is an ageless scientific question, a “grand challenge” of truly epic proportions. It is such a large problem that we are tempted to pretend that we are not interested, and rather focus on more mundane issues.

Yet despite its difficulty there are many beneficial applications to be had along the way. A machine with human-like pattern classification ability can be scaled up to search large amounts of data, or detect anomalies and attacks on computer systems. A model that accurately reflects the sentiments of our adversaries can help us predict their actions, or perhaps avoid creating enemies altogether.

The human brain is the most complex object in the known universe. Hordes of scientists are actively engaged in studying its various parts. For example, the annual conference of the Society for Neuroscience draws over 30,000 people presenting on over 1,000 topic areas.

All this knowledge — beyond the capacity of any individual to comprehend — must be integrated into a unified model. Ultimately, the complete model of human cognition cannot exist as an idea in one person’s mind. Rather, it will be an information structure held in a large computer system.

The goal of this project is to build the scaffolding for that system. Around us wait powerful tools for this task: large parallel computing, big data processing, model reduction techniques, uncertainty quantification, and visualization. If we wield them, we can foster a scientific breakthrough.

We seek cooperation from the neuroscience community to input models in a computable format: sets of differential equations bundled inside “parts.” Our tool will both simulate the model and analyze its structure. We hope to succeed where other neuroinformatics efforts have failed by making simulation easy and by adding value for our contributors.

Incremental Learning for Automated Knowledge Capture 151346

Year 2 of 3

Principal Investigator: Z. O. Benz

Project Purpose:

People responding to high-consequence national security situations need tools to help them make the right decision quickly. The dynamic, time-critical, and ever-changing nature of these situations, especially those involving an adversary, requires models of decision support that can dynamically react as a situation unfolds and changes. Automated knowledge capture is a key part of creating individualized models of decision making in many situations because it has been demonstrated as a very robust way to populate computational models of cognition. However, existing automated knowledge capture techniques only populate a knowledge model with data prior to its use, after which the knowledge model is static and unchanging. In contrast, humans, including our national security adversaries, continually learn, adapt, and create new knowledge as they make decisions and witness their effect. This artificial dichotomy between creation and use exists because the majority of automated knowledge capture techniques are based on traditional batch machine learning and statistical algorithms. These algorithms are primarily designed to optimize the accuracy of their predictions and are only secondarily, if at all, concerned with issues such as speed, memory use, or ability to be incrementally updated. Thus, when new data arrives, batch algorithms used for automated knowledge capture currently require significant recomputation, frequently from scratch, which makes them ill-suited for use in dynamic, time-critical, high-consequence decision-making environments.

A Comprehensive Approach to Decipher Biological Computation to Achieve Next Generation High-Performance Exascale Computing

151347

Year 2 of 3

Principal Investigator: C. D. James

Project Purpose:

The human brain (volume=1200 cm³) consumes 20 W and is capable of performing $>10^{16}$ operations/s. Current supercomputer technology has reached 10^{15} operations/s, yet it requires 1500 m³ and 3 MW, giving the brain a 10^{12} advantage in operations/s/W/cm³. Thus, to surpass exascale computation (10^{18} operations/s) with reasonable power and volume, two achievements are required: 1) improved understanding of computation in biological tissue and 2) a paradigm shift towards “neuromorphic” computing where hardware circuits are given architectures and information processing strategies that mimic neural tissue. To address progress toward the first achievement, we will interrogate corticostriatal networks in mouse brain tissue slices. These networks are crucial to processing massive amounts of information (sensory, motor, reward, cognitive inputs) during decision-making, and our work will help to identify key information processing elements that enable the collection and synthesis of such information into actionable decisions. Specifically, we will work with our collaborators at the University of New Mexico to characterize the frequency sensitivity of memory storage (long term depression [LTD]) in these networks. Elements that will be quantitatively measured include signal thresholding and spike-timing and frequency-dependent changes in synaptic connections. To address progress toward the second achievement, we will instantiate biological computing elements found through our first effort into a microfabricated neuromorphic hardware circuit with demonstrated low-power and reconfigurable function characteristics. Memristor devices will be fabricated in the Microsystems and Engineering Science and Applications (MESA) facility in consultation with Hewlett Packard and our internal collaborators. Memristors will then be incorporated into test structures (e.g., digital-to-analog converter, dynamic filter, stable amplifier) where the reconfigurability and low-power nature of the memristor devices will provide unique benefits.

Systems Biology in 3D: Monitoring and Modeling the Dynamics of *Francisella tularensis*-Associated Granuloma Formation

151348

Year 2 of 3

Principal Investigator: S. M. Brozik

Project Purpose:

According to recent research findings, formation of granulomatous-necrotic lesions in mice infected with *Francisella tularensis* (Ft), a category-A bioterrorism agent, may serve to control and regulate early stages of infection. Traditional sample-sacrifice experimental protocols have enabled significant insight into the cellular composition of these granulomas; however, an understanding of multiscale mechanisms and host-pathogen interactions that mediate Ft-related granuloma formation is lacking. Specifically, we are exploring: 1) the functional role of macrophages and effector molecules (e.g., nitric oxide [NO] and reactive species) in formation and establishment of an unfavorable granulomatous-microenvironment and 2) the intracellular response of Ft within the granuloma-associated microenvironment.

Existing experimental methods do not capture the dynamics of host-pathogen intra/intercellular events that lead to 3D granulomatous structures; thereby, preventing full exploration of the role of these structures on immunopathogenic outcomes of Ft. Using a multidimensional systems-biology approach, we will investigate the correlation between intracellular-scale events (e.g., chemokine-mediated cell recruitment, NO biosynthesis) and granuloma formation. Further, we will explore the impact of granulomatous structures on Ft viability and dissemination during infection. We will develop an experimental platform to enable real-time dynamic profiling of Ft infection of host mononuclear cells in a 3D environment. The platform will consist of a 3D microfluidic porous collagen-based scaffold that will serve as a synthetic extracellular matrix (ECM) for interrogating host cell responses to pathogen exposure in an ex vivo microenvironment. This platform will enable real-time optical and electrochemical monitoring of Ft-infection and granuloma formation events. Quantitative and semi-Quantitative spatio-temporal observations will be used to develop a theoretical model of this important host response mechanism, which will enable us to explore and develop new hypotheses regarding the relative kinetics of host-response and effective protection during Ft infection.

Reverse Engineering the Host-Virus Interaction using an Artificial Host Cell 151349

Year 2 of 3

Principal Investigator: D. Y. Sasaki

Project Purpose:

The goal of this project is the development of a model system for understanding the entry pathway of pathogenic (Henipah) viruses. Even as a primary threat to national security, pathogenic viral entry pathways remain poorly defined. Strategies for detection and therapy of viral infection would greatly benefit from fundamental understanding of the mechanisms used for the entry event. While much has been learned about the biochemistry of pathogen invasion from studying interactions with host-cells, the complexity of cellular processes makes it difficult to isolate the fundamental requirements of infection. The role of receptor clustering, lipid composition, and membrane phase in viral entry are extremely difficult to characterize using a live cell approach. As a complement to such studies, we propose to develop model systems to detect pathogen invasion by recreating the essential early events of infection by enveloped viruses. Our artificial host will consist of a supported lipid bilayer (SLB) that will mimic the chemistry, structure, and mechanics of cellular membranes. The structure and mechanics of the membrane will be tailored by the use of incorporated lipid components to create specific phases, polymer cushions to minimize substrate interactions, and lipid domain architectures to mimic raft-like assemblies in cells, which are known sites of viral entry. Chemistry will be tuned to enhance affinity (electrostatics, sterol content) and specific coupling (receptor proteins) of the viral particles. Scanning point mutation libraries will allow us to probe specific amino acid sites on the Nipah virus G stalk region to gain insight on structure and chemistry of the viral ligands on fusion. Fusion events will be followed using total internal reflectance fluorescence (TIRF) microscopy to capture hemi-fusion and full-fusion processes. Using this minimalistic approach we hope to provide a detailed understanding of the mechanisms of enveloped virus fusion and facilitate new methods for potential rapid screening of pathogenic agents.

Biomimetic Lung Toxicity Screening Platform (bioMIMIC)**151350****Year 2 of 3****Principal Investigator:** A. Hatch**Project Purpose:**

While the use of engineered nanomaterials continues to burgeon, questions relating to potentially harmful human health effects linked to nanomaterial exposure have not been convincingly addressed. Animal models are considered the gold standard for physiological insight into nanomaterial toxicity, but they are not feasible as first-line screening tools due to high study costs and potential interspecies variability. Conversely, single-phenotype Petri dish studies can provide cellular level toxicity readouts in a scalable manner, but seldom represent integrated tissue level physiological responses. To overcome these deficiencies, the National Research Council's report entitled, "Toxicity Testing in the 21st Century: a Vision and a Strategy," has identified a critical need for scalable, physiologically relevant in vitro tissue mimics that can minimize or replace animal toxicity studies while providing insight into the human effects of nanomaterial exposure. The goal of this project is to develop a microfluidic, cell-based platform that will enable the detailed study of integrated toxicity responses induced by exposure to engineered nanomaterials. We will generate the tissue mimic by creating an ordered multi-phenotypic construct that will provide an accurate representation of the alveolar-capillary interface found in the lung. Toxicity responses to well-characterized nanomaterial exposure will be quantified using commercial and Sandia techniques.

Descriptions and Comparisons of Brain Microvasculature via Random Graph Models

151368

Year 2 of 2

Principal Investigator: R. Schiek

Project Purpose:

Brain tissue includes a close interaction of neurons, glial cells, and microvasculature. The proposed project, in collaboration with Cornell University, will increase knowledge of brain microvasculature by extracting maps of the microvasculature from 2-photon optical 3D imagery, describing such maps as random graphs, and developing statistical tools for comparing the graphs.

The project will use microscopy methods developed at Cornell University for the study of micro strokes.

The resolution is approximately one micron laterally and somewhat less in depth to a maximum depth of 1 millimeter which for mouse cortex is nearly full thickness. Three activities are being pursued.

1. Develop computational methods to extract complete maps of the cortical microvasculature from 3D images based on angiographic medical imaging techniques.
2. Develop methods for computing generative random-graph models of those map based on estimating the probability laws (or the parameter in the probability laws) that generate the random graphs. This requires estimation algorithms for space-dependent graph structures since the cortex changes with depth below the surface (i.e., cortical levels) and is organized laterally in columns. Furthermore, the map obtained from pursuit number one will have errors (both true edges missing and false edges inserted) so a model for errors (possibly with unknown parameters to be estimated) is required. Finally, edges are marked with the physical length and diameter of the corresponding vessel and generative models for these marks, possible correlated with the graph itself are desirable.
3. Develop statistical tests for comparing graphs in order to determine whether a particular chronic intervention leads to a change in the microvasculature. The interventions could be therapeutic (e.g., a drug or neuro stimulator) or environmental (e.g., chronic stress).

Summary of Accomplishments:

The research is concerned with using electrical engineering tools in neuroscience: Circuit model of the neurovascular network, abstract descriptions of vascular networks, and determination of flow speeds in the microvasculature from video 2-photon laser scanning microscopy. Thus far, the project has produced the following:

- Developed computational models of neurovascular networks
- Developed techniques for refining graphs
- Developed the ability to derive the underlying vascular graph structure and flow properties, by making use of archival data of mouse cortex blood flow.

Significance:

An important aspect of this work is the theoretical description of vascular graphs and how they are compared and completed. While focusing on vascular systems, this underlying work applies to information graphs in general and has applications in network dynamics and resiliency and addresses DOE's interest in scientific innovation and discovery.

Refereed Communications:

T.P. Santisakultarm, N.R. Cornelius, N. Nishimura, A.I. Schafer, R.T. Silver, P.C. Doerschuk, W.L. Olbricht, and C.B. Schaffer, "In Vivo Two-Photon Excited Fluorescence Microscopy Reveals Cardiac- and Respiration-Dependent Pulsatile Blood Flow in Cortical Blood Vessels in Mice," *American Journal of Physiology Heart and Circulatory Physiology*, vol. 302, pp. 1367-1377, April 2012.

CVD Encapsulation of Mammalian Cells for Hazardous Agent Detection 151375

Year 2 of 3

Principal Investigator: J. C. Harper

Project Purpose:

In order to detect chemical and biological threats both on the battlefield and in civilian life, development of portable, robust detection systems capable of real-time identification of chemical and biological agents are needed. Living cell-based sensors, described as the equivalent of canaries used to detect toxic gases in mines, have proven effective as sensitive and specific detectors, capable of near real-time detection. However, living cell-based sensors require frequent replenishment with new cells, typically every 1–7 days, due to the sensitivity of the cells to the ex-vivo environment. Incorporation of living cells within a biocompatible matrix that provides mechanical protection while maintaining access to the external environment may facilitate the development of long-term stable cell-based biosensors. We are exploring the use of a novel Chemical Vapor into Liquid (CViL) deposition process for whole cell encapsulation in silica. The CViL technique exploits the high vapor pressure of common silica alkoxides for precise control over silica delivery and resultant silica shell deposition. As a model system for whole cell encapsulation, we use *S. cerevisiae* engineered with an inducible beta galactosidase system to measure response to a model analyte. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) are employed to characterize silica within cell samples which have undergone CViL. Scanning electron microscopy, energy dispersive spectroscopy (SEM-EDS) data shows Si at the cell surface and not in the background. Fluorometry experiments demonstrate that cells which undergo CViL treatment are responsive to analyte on par with the response of control cells stored in media. These results indicate that living cells treated by Si CViL are encapsulated within amorphous silica and that the cells remain viable and responsive. This advance may hold significant promise in producing cell-based biosensors practical in a wide range of environments, including unstable regions with limited infrastructure.

In Vitro Construction of Complex Random Peptide Libraries Displayed on Virus-Like Particles for Use in Rapid Response to Emerging Pathogens and Biowarfare Agents

151379

Year 2 of 3

Principal Investigator: C. E. Ashley

Project Purpose:

Virus-like particles (VLPs) of MS2 bacteriophage self-assemble from 180 copies of a single coat protein into a monodisperse, 28-nm icosahedron that is highly tolerant of multivalent peptide display and can be rapidly loaded with nearly any cargo of interest. MS2 VLPS are, therefore, well suited for use as potentially immunogenic vaccines against viral or bacterial pathogens and as targeted nanocarriers capable of delivering therapeutic agents to pathogenic bacteria or virally infected mammalian cells with high specificity. The utility of MS2 VLPs in vaccine development and targeted delivery applications can be greatly enhanced through their development as a platform for random peptide display, which, upon synthesis of a complex library, will enable identification of peptide sequences with an affinity for any material. The goal of our research is to first develop a complex random peptide library entirely in vitro using MS2 VLPs as a display platform. In vitro VLP display is entirely novel and will enable the convenient production of high complexity libraries (10^{11} – 10^{13} members) and will make library construction and affinity selection amenable to automation. We will then utilize monoclonal antibodies (mAbs) against Nipah virus to affinity-select VLPs that display peptide mimotopes. We will test the ability of selectants to elicit a neutralizing antibody response using in vitro neutralization assays. We will also identify VLPs capable of delivering therapeutic RNAs to NiV-infected cells using either viral glycoproteins (e.g., NiV-G) or receptors necessary for viral entry into host cells (e.g., ephrin B2) in affinity selection experiments. To inhibit the production and spread of biosafety level 2 pseudoviruses in vitro, we will encapsidate siRNAs that induce sequence-specific degradation of viral mRNA within targeted VLPs. VLP technology promises to be a remarkably powerful, universal technology that will enable rapid, cost-effective identification of vaccine candidates and targeted nanocarriers in order to effectively combat infectious disease.

The PI is a President Harry S. Truman Fellow.

Electrokinetic Measurements of Surfaces

155553

Year 2 of 2

Principal Investigator: B. Simmons

Project Purpose:

As microfluidic devices have used more and more nanoporous membranes and more interfacial phenomena and incorporated more novel materials, the linear models of electrokinetic phenomena have failed, and we have, to date, been unable to predict a number of common nonlinear electrokinetic phenomena. Interfacial potential is a central component of countless membrane-based and microfluidic processes, and constitutes one of the primary ways by which electrolytes and interfaces are characterized. High-charge surfaces are postulated to change water structure near interfaces, with some reports claiming that these changes occur over microscopic (rather than nanoscopic) length scales. Our work features interfacial characterization of Nafion — a high-surface-charge density polymer associated with multiple anomalous water physics observations — crystalline halides, and hafnium oxide, a high-dielectric-constant material used extensively in microfabrication. By combining these measurements with classical materials (silica series and silver iodide), these measurements inform a holistic model of mission-critical interfacial phenomena. Our phase-sensitive streaming potential has provided the most extensive and low-noise streaming potential data to date, putting us in a unique position to infer material properties and link them to other fundamental constants.

Summary of Accomplishments:

A streaming potential tool was developed to facilitate interfacial characterization of materials in conjunction with surface spectroscopy and atomic force microscopy (AFM) characterization. Analytical and numerical techniques were applied to electrokinetic flows with attention to permittivity and viscosity variations in the electrical double layer. We have designed, constructed, and implemented a flat plate streaming potential cell. The cell was designed in Pro/E and machined from a combination of polycarbonate and aluminum. The polycarbonate forms the inner part of the cell — a small amount of the surface is wetted forming reservoirs at the up and downstream ends of the cell. The aluminum pieces, in conjunction with 1=4.20 hardware, form a clamp to seal the polycarbonate pieces. Aside from machining the polycarbonate and aluminum pieces for the direct use by the streaming potential cell, several other support structures were designed and built. These pieces are used to cut out gasket and spacer shapes from silicone and Teflon.

Fixturing of pressure, flow, and voltage input/monitoring was accomplished by boring small holes in 8-32 nylon screws and inserting the appropriate conduit. For flow, a ground 16-gauge needle was pressed into the hole, forming a seal. For voltage, a platinum wire was epoxied in a similar hole; the same gluing technique was used to insert a small gauge steel tube to measure pressure. A pressure test was executed to determine the maximum sealing pressure by the cell and was found to be in the neighborhood of 100 psi, well above the maximum pressure at which the device is to be run. A new differential pressure transducer was implemented. Also, the streaming potential device was connected to a syringe pump and labview, and data collected for plain glass slides.

Significance:

The numerical experiments provide strong insight into the behavior of a fluid near an interface with a high field, but it is also instructive to construct analytical approximations. Fluids are notoriously difficult to model, and most of the descriptions that are available for permittivity are obtained either

through empiricism or coarse-graining of the physics by neglecting interactions between molecules. Furthermore, these models typically account for one type of perturbation to a bulk solution, namely, either local field dependence or local concentration dependence. The capabilities developed in this project, enabling increased understanding of fluidic interfaces, are important to current microfluidic device functioning, but also contribute to scientific understanding, thereby laying a portion of the groundwork for forthcoming technological innovation pertaining to this area of DOE interest.

Refereed Communications:

V.T. Tandon and B.J. Kirby, "Ambient Pressure Effects on the Electrokinetic Potential of Zeonor-Water Interfaces," *Journal of Colloid and Interface Science*, vol. 361, pp. 381-387, September 2011.

Luminescent Lanthanide Reporters for High-Sensitivity Novel Bioassays

157690

Year 2 of 3

Principal Investigator: M. Anstey

Project Purpose:

Biological imaging and assay technologies rely on fluorescent organic dyes as reporters for a number of interesting targets and processes. However, limitations of organic dyes such as small Stokes shifts, spectral overlap of emission signals with native biological fluorescence background, and photobleaching have all inhibited the development of highly sensitive assays. The polymerase chain reaction, (PCR), is a current work-around for increasing sensitivity, but PCR can introduce bias into the sample and complicate data interpretation. In addition, a need is arising for identifying multiple targets for biomarker discovery or pathogen detection from a bioterrorist attack. These multiplex assays are currently expensive and complex, utilizing microarray plates or multiwavelength excitation/emission detection systems, which limit their application. What is needed is a new type of fluorescent moiety that offers improved properties over organic dyes, enables cost-effective multiplexed analysis, and provides opportunities for novel high-sensitivity bioassays.

To overcome the limitations of organic dyes for bioassays, we propose to develop lanthanide-based luminescent dyes and demonstrate them for molecular reporting applications. This relatively new family of dyes was selected for their attractive spectral and chemical properties. Luminescence is imparted by the lanthanide atom and allows for relatively simple chemical structures that can be tailored to the application. The photophysical properties offer unique features such as narrow and non-overlapping emission bands, long luminescent lifetimes, and long-wavelength emission, all of which enable significant sensitivity improvements over organic dyes through spectral and temporal gating of the luminescent signal.

Growth in this field has been hindered due to the necessary advanced synthetic chemistry techniques and access to experts in biological assay development. At Sandia, a multidisciplinary partnership between chemistry, biology, and engineering is easily formed and will allow this project to advance the state of the art.

Pathogenicity Island Mobility and Gene Content 158185

Year 2 of 3

Principal Investigator: K. P. Williams

Project Purpose:

Key goals towards national biosecurity include improved methods for diagnosing pathogens (natural or engineered), predicting their emergence, and developing vaccines and therapeutics. These goals could be achieved, in part, through a comprehensive analysis of bacterial genes that promote pathogenicity and the mobile DNA elements (pathogenicity islands) where such genes typically reside. Our current knowledge of bacterial pathogenicity genes is extremely limited, and typically based on painstaking laboratory study. In this project, we are pursuing the development of an automated system to identify islands as soon as genomes are posted at GenBank, and to analyze island gene content and mobility. The resulting island database will address a cyber-infrastructure need and moreover provide a short list of potential pathogenicity genes in a new pathogen, enabling deeper bioinformatic island analysis that may allow positive identification of novel pathogenicity genes.

Multiple islands can accrue throughout a genome to combinatorially enhance or modulate pathogenicity. Diverse islands can even appear in tandem arrays at genomic integration hotspots, a configuration promoting inter-island recombination events that may produce new islands with novel gene combinations. The proposed database will enable an in-depth analysis of island genomic sites and arrangements, as well as their phylogenetic distributions, to shed light on how island mobility, evolution, and functional cooperation promote pathogenicity.

Pathogenicity islands are poorly understood and present unique challenges for study, but meeting these challenges to better understand island nature, especially learning how to identify the cryptic pathogenicity genes they may carry, has potentially tremendous payoffs for human health, microbial ecology, and biosecurity.

Production of Extremophilic Bacterial Cellulase Enzymes in *Aspergillus niger* 158186

Year 2 of 3

Principal Investigator: J. M. Gladden

Project Purpose:

Lignocellulosic biofuels hold great promise for dramatically reducing the US dependence on foreign oil. These technologies aim to convert sugars derived from plant biomass feedstocks into biofuels. Current biofuel processing configurations operate under mesophilic conditions, but there is a push toward thermophilic conditions for a variety of reasons, including reduced contamination, more efficient fuel recovery, better enzyme kinetics, and higher metabolic rates, all of which would significantly reduce costs for biofuel production.

A few companies have already begun developing thermophilic biofuel production hosts, but have yet to complete the thermophilic bioprocessing configuration by developing a cellulase cocktail. The thermophilic biofuel system offers several advantages over current mesophilic approaches, most importantly the significant reduction of opportunistic microbial infection. Commercial cellulase cocktails are derived from filamentous fungi that produce very high enzyme titers, essential for commercialization. Unfortunately, these enzymes are inactive at high temperatures. Thermophilic bacteria produce highly stable thermophilic cellulases and are an excellent alternative. However, bacteria generally produce low titers of these enzymes, an order of magnitude too low. To overcome this barrier, we will attempt to develop a high-titer thermophilic bacterial cellulase cocktail by expressing these bacterial enzymes in a commercial filamentous fungal host — *Aspergillus niger*.

Our proposed approach would represent the first time an entire bacterial pathway was reassembled in a filamentous fungus. We aim to produce the first high-titer thermophilic cellulase cocktail with the potential for significantly reducing the costs of commercial cellulosic biofuels. Expression of bacterial enzymes in filamentous fungi has historically proven difficult because these enzymes are quite foreign to fungi, which leads to poor expression and inhibitory modifications. We have devised a multipronged approach to overcome these barriers, including fusion to fungal enzymes and extensive engineering of the bacterial genes to make them more compatible with fungi.

Intra-Membrane Molecular Interactions of K⁺ Channel Proteins: Application to Problems in Biodefense and Bioenergy

158410

Year 2 of 3

Principal Investigator: E. Moczydlowski

Project Purpose:

The goal of this project is to develop new methods to measure and analyze the structural basis of K⁺ channel tetramer stability for applications in biodefense and bioenergy. Ion-selective channel proteins are key effectors of electrophysiological processes linked to cell membrane signal transduction, mechanisms relevant to microbial pathogenesis and bioenergy production. The aqueous pore of most channel proteins is formed at the central interface of identical or homologous subunits of a torus-like complex embedded within a lipid membrane. All known highly K⁺-selective channels from viruses to humans share a structurally homologous pore domain, which is a complex of four subunits (homo- or hetero-tetramers). Since integrity and stability of such multisubunit protein complexes is required for assembly and function of most channels, molecular mechanisms underlying intra-membrane protein-protein interactions are of fundamental interest.

The scientific problem addressed by this project may be described as follows:

- What is the molecular basis of tetramer stability of K⁺ channel proteins?
- How does tetramer stability correlate with ion discrimination, binding affinity, and conductance?
- How do channel functions of ion selectivity, open-closed gating dynamics, signaling, and pharmacology depend on inter-subunit interactions?

Despite intensive research on K⁺ channels, the relationship between tetramer stability and channel function remains virtually unexplored. It is known that lowering extracellular K⁺ results in loss of function of many K⁺ channels; however, the molecular basis of this phenomenon is poorly understood. The scientific challenge is to develop new approaches to measure, analyze, and engineer the molecular specificity and energetic basis of intra-membrane subunit-subunit interactions of K⁺ channels. This knowledge can be applied to discovery of new classes of small molecules that disrupt channel function for treatment of human diseases and suppression of pathogenic microbes. It can also be used to design highly stable K⁺ channels for engineering of hybrid material nanodevices in the emerging field of bionanoelectronics.

Functional and Robust Asymmetric Polymer Vesicles

158478

Year 2 of 3

Principal Investigator: W. F. Paxton

Project Purpose:

In a living cell, the directional exchange of matter, energy, and information across the membrane is facilitated primarily by transmembrane proteins (TMPs) that are asymmetrically distributed and oriented. Mimicking this asymmetry and function in synthetic hybrid systems is a longstanding challenge in biomolecular and materials science. We seek to understand the principles that govern the reconstitution of TMPs into robust matrices in order to create vesicles that are both radially and axially asymmetric. We intend to: 1) explore systematically the parameters that govern vectorial insertion of TMPs in robust biomimetic environments and 2) use what we learn to create radially and axially asymmetric hybrid constructs that could be used to regulate the transport of charge in energy production and storage systems and understand signal transduction at immunological synapses between cells and model biomimetic membranes.

Many reports demonstrate that TMPs can be reconstituted into synthetic vesicles and that they retain their activity after reconstitution, yet none have provided a general strategy for controlling the orientation of protein insertion. Furthermore, lipid-based vesicles (liposomes) typically used in reconstitution experiments lack the chemical and mechanical stability required for materials science applications. Polymer-based vesicles (polymersomes) developed over the past decade possess many of the desirable properties of liposomes, while at the same time exhibit remarkable stability relative to their lipid-based counterparts. Our approach to integrating TMPs in biomimetic environments capitalizes on recent developments in: 1) preparing polymersomes, 2) reconstituting TMPs in vesicle assemblies, and 3) synthetic vesicle fusion to prepare robust hybrid structures that are both radially and axially asymmetric. The successful execution of the proposed work will bring new fundamental understanding to the role intermolecular interactions play in protein insertion mechanisms. We anticipate that our approach will afford a versatile platform for integrating TMPs into robust scaffolds that will allow the rational design of an entirely new class of asymmetric biomimetic materials.

Mechanism of Fusion of Pathogenic-Enveloped Viruses with the Endosomal Membrane

158832

Year 1 of 3

Principal Investigator: M. S. Kent

Project Purpose:

Pathogenic membrane-enveloped viruses including flaviviruses, arenaviruses, and paramyxoviruses cause devastating infectious diseases (e.g., hemorrhagic fever, encephalitis) and pose major biodefense threats. For these viruses, fusion of the viral membrane with the cellular endosomal membrane is essential for viral replication and infectivity. Fusion of the two membranes is driven by pH-dependent conformational changes of a dedicated protein, called E in flaviviruses. Crystal structures have been determined for the pre-fusion and post-fusion states of E, but only for truncated mutants lacking important flexible and membrane-spanning portions. Thus, a huge gap in knowledge exists regarding conformational changes of E upon binding to the endosomal membrane and during the intermediate stages of fusion, and also regarding the mechanism by which E anchors into the endosomal membrane. This project is attempting to address: 1) E protein membrane-bound structure and 2) E protein anchoring to endosomal membranes.

It is very difficult to resolve conformational changes of membrane-bound proteins because crystallization of proteins in the membrane-associated state is extremely challenging, and cannot capture structural transitions that occur as a function of solution conditions. This explains the current gap in knowledge for the fusion process. However, at Sandia, we have developed a capability to capture such structural transitions based on neutron reflectivity (NR) and fluorescence energy transfer (FRET). We will perform NR analysis of membrane-bound E as a function of pH, which will provide global structural information. Specific local information (i.e., distances between specific residues or between particular residues and the membrane) will be supplied by FRET. Site-specific mutation of E protein will be performed to introduce labels for FRET, whose effects on function will be screened in-vitro and in live-cell fusion assays. We will also resolve the interactions that anchor the tip of E into the endosomal membrane using molecular simulations and atomic force microscopy measurements.

Identification of Host Response Signatures in Mouse Models of Crimean-Congo Hemorrhagic Fever Virus Infection

158834

Year 1 of 1

Principal Investigator: S. Branda

Project Purpose:

Effective biosurveillance and outbreak mitigation requires efficient and reliable distinction between infected vs. healthy individuals to enable rational use of scarce, invasive, and/or costly countermeasures (diagnostics, therapies, quarantine). Screening based on direct detection of the causative pathogen can be problematic, because culture- and probe-based assays are confounded by unanticipated pathogens (e.g., deeply diverged, engineered), and readily accessible specimens (e.g., blood) often contain little or no pathogen, particularly at pre-symptomatic stages of disease. Thus, in addition to the pathogen itself, one would like to detect infection-specific host response signatures in the specimen, preferably ones comprised of nucleic acids (NA), which can be recovered and amplified from tiny specimens (e.g., a single cell). Proof-of-concept studies have not been definitive, however, largely because use of suboptimal sample preparation and detection technologies has precluded comparative analysis of clinical specimens with sufficient specificity, sensitivity, comprehensiveness, and throughput.

For purposes of pathogen detection, Sandia has developed novel molecular biology methods that enable selective isolation of NA unique to, or shared between, complex samples, followed by identification and quantitation via Second Generation Sequencing (SGS). Our central hypothesis is that variations on this approach will support efficient identification and verification of NA-based signatures of infectious disease. We will re-engineer Sandia's sophisticated sample preparation pipelines and develop new SGS data analysis tools and strategies, in order to pioneer use of SGS for identification and verification of NA signatures of disease. Proof-of-concept studies will be carried out using samples derived from pathogen-infected non-human primates (NHP). This work will provide a strong foundation for large-scale, highly efficient efforts to identify and verify disease-specific NA signatures in human populations.

Summary of Accomplishments:

The primary goal of this project is to develop and demonstrate a powerful and efficient new approach for discovery of host-derived NA signatures of infectious disease.

Blood specimens (white blood cells [WBC] and plasma) were collected from three NHP exposed to aerosol containing *Yersinia pestis* CO92. From each NHP, we received WBC and plasma from a pre-infection and 2-3 post-infection bleeds. From each sample, we extracted RNA, generated SGS-ready cDNA, and used novel molecular suppression methods to fractionate the cDNA libraries for highly efficient SGS analysis.

We identified 219 NHP genes that showed infection-induced changes in expression that were statistically significant ($p < 0.05$) and highly correlated ($> 90\%$) across the three NHP. Use of molecular suppression methods enabled reliable measurement of low-level gene expression, which in turn enabled identification of an additional set of genes repressed upon infection.

The differentially expressed genes included: 1) genes that perform functions known to be elicited by bacterial infection (e.g., Toll-like receptor pathways, iron metabolism), 2) genes that perform functions

not previously linked to infection (e.g., proteolysis of proteins involved in Alzheimer's disease, regulation of intracellular potassium), and 3) genes of unknown function.

Gene network analyses suggest that many of the represented pathways are interconnected through transcription factors. In several cases, a single transcription factor appears to be responsible for activating many genes and pathways simultaneously. In this sense, response to infection appears to be largely coordinated by these “master regulator” transcription factors (e.g., AP-1, IRF7).

With only three subjects in this study, there was not enough statistical power in the gene expression patterns to generate defensible prognostic or predictive classifiers for disease diagnosis. However, our work can serve as a guide for targeting of particular pathways and features in building diagnostic classifiers.

Significance:

We have carried out an in-depth analysis of host transcriptional responses to infection in the blood of NHP exposed to aerosolized *Y. pestis* CO92. Our results provide new and valuable insight into the molecular mechanisms of host defense against a fully virulent bacterial pathogen of importance to the biodefense interests of DOE, DHS, and other agencies. Our study serves as a strong foundation for development of assays and devices enabling early diagnosis of *Y. pestis* infection based on blood transcriptome signatures, which will significantly improve our ability to detect and effectively respond to both natural and intentionally initiated infectious disease outbreaks.

Utilizing Biocomplexity to Propagate Stable Algal Blooms in Open System — Keeping the Bloom Going

158835

Year 1 of 3

Principal Investigator: E. T. Yu

Project Purpose:

Our project addresses the most significant barrier facing commercialization of algal biofuels — sustained high biomass producing algae cultures in open ponds. Cultivation of algae in open ponds — the most economically viable option for biomass production — suffers from instability and inability to sustain high production rates. Although higher algae productivities are regularly touted ($30 \text{ g/m}^2/\text{day}$), established algae facilities can only produce $\sim 2 \text{ g/m}^2/\text{day}$. Achieving biological stability (limiting invasion of undesirable species, grazers, and pathogens) is, therefore, critical in mass algae production. In nature, microorganisms exist as consortia of functionally specialized and interacting individuals that collectively adapt to dynamic environmental cues, resulting in stability (robustness against environmental insult). We propose to exploit biocomplexity to develop a fundamental understanding of naturally stable algae consortia and to apply this understanding to developing stable high biomass producing “artificial” consortia that recreates the stability of natural assemblage but with the yield of the production strain.

Our innovative approach is to investigate naturally stable communities as complex adaptive systems whose stability emerges from collective nonlinear interactions among autonomous agents and their environment. We plan to: 1) identify the aquatic species in naturally stable algal communities and examine community structure as a function of system perturbations, 2) identify critical functions that stabilize the community by constructing and interrogate representative mixed cultures in vitro for functional validation, 3) develop agent-based models to understand the relationship between biocomplexity and stability, and 4) spiral around computational and experimental perturbation studies to converge on stability promoting factors (bench scale) followed by pond demonstration at scale.

Using High-Performance Computing to Examine the Processes of Neurogenesis Underlying Pattern Separation/Completion of Episodic Information

158836

Year 1 of 3

Principal Investigator: M. L. Bernard

Project Purpose:

One of the most perplexing questions pertaining to our understanding of memory concerns how the brain distinguishes between patterns of related events that are separated in time. Understanding this question could have far-ranging impacts with regard to Sandia's ambition to establish next-generation memory processing and pattern classification systems. Studies have provided evidence that the dentate gyrus (DG) processes highly convergent information from cortical regions of the brain. This information is further processed and associated within the CA3 subarea of the hippocampus to help distinguish patterns of events. Studies suggest this process is aided in the DG through neurogenesis. Neurogenesis may serve to support the process of discriminating (separating) patterns by reducing similarity between new and older event information. It may also support pattern completion by increasing associations between temporally similar events, which are then transmitted to the CA3 area of the hippocampus as sparse inputs. Unfortunately, little is known about how the underlying processes of these subareas work as a system. Also, the computational models that have been developed tend to have very reduced representations of the actual neural processes, greatly diminishing their generalizability to actual brain functioning. Accordingly, we propose to neurocognitively model the population dynamics of a fully representative, neurogenesis association system in order to examine how these subareas enable pattern separation and completion of information in memory across time as associated experiences.

Only 15 years ago, most neuroscientists believed that the brain did not add new cells over the course of its lifetime. While initially controversial, it has been increasingly appreciated that neurogenesis occurs in certain regions of the brain, with debate having now turned to the functional role of neurogenesis. This proposed research would place Sandia at the forefront of one of the most significant paradigm shifts in the history of neuroscience, which could have major ramifications for efforts to emulate neural processes in computer code.

A Novel Nanobiotechnological Approach for Controlling and Enhancing Cognitive Function

158847

Year 1 of 1

Principal Investigator: G. Bachand

Project Purpose:

The ability to temporarily and selectively silence neurotransmitter expression in specific regions of the brain has the potential to revolutionize our understanding of cognitive function. Presently, cognitive function is correlated with neural activity using electroencephalography (EEG) or a variety of imaging techniques (e.g., fNIRs, fMRI, PET, etc.). While useful, these techniques are severely limited with respect to spatial and temporal resolution, and simply provide statistical correlations between large populations of neurons and a specific cognitive response. A more thorough and systematic understanding of how specific cell types function within and among the different brain regions necessitates new and innovative approaches that can overcome these limitations. Emerging technologies such as RNA-interference offer the ability of temporarily knocking-out gene expression, which, if applied to neurons, may be used to directly link cognitive function to specific cells via molecular-level control of cellular physiology. The fundamental technical challenge of this approach is the ability to deliver and controllably release small-interfering RNA (siRNA) in specific neural cells within a larger complex network.

We pursue a novel approach for using radiofrequency (RF)-responsive, engineered nanoparticles to deliver and release siRNA in neural cells, thereby “silencing” the production of specific neurotransmitters. This approach offers the unique ability to test defined hypotheses with respect to the cell function and connectivity within the larger brain architecture. For example, it would be possible to temporarily inhibit dopamine synthesis in the substantia nigra region of the brain and directly characterize the resulting change in cognitive response. Key to this approach, however, is the targeted delivery and controlled release of siRNA in neurons. We will use porous, iron oxide nanoparticles (PIONs) as the siRNA delivery vehicles based on a number of unique advantages including: increased loading in particle pores, biostability/biocompatibility, ease of functionalization for targeted delivery, enhanced contrast in advanced imaging (e.g., MRI), and responsiveness to RF radiation for programmed siRNA release.

Summary of Accomplishments:

During the initial phase of this work, we developed methods to synthesize nanosized PIONs for siRNA delivery in neurons. From these methods, we assembled a library of PIONs with varying sizes, aspect ratios, porosities, and magnetic susceptibilities. PIONs were characterized using scanning electron microscopy, transmission electron microscopy, and dynamic light scattering. The zeta potential of the different PIONs was also measured. Key characteristics that were achieved here included: 1) sizes of <500 nm, which enables cellular uptake in the absence of phagocytosis and 2) aspect ratios of ~3–4, which have been previously shown to increase the rate of uptake in neurons. We also demonstrated the ability to locally heat PIONs using RF radiation.

We then developed methods for making the PIONs both colloiddally stable and biocompatible. PIONs were coated with a synthetic lipid bilayer using a vesicle fusion approach where PIONs fuse with small unilamellar vesicles and form a continuous lipid seal around the particle. The zeta potential of the PIONs was measured before and after lipid coating and this measurement demonstrated that the particles were indeed encapsulated. In addition, fluorescence co-localization studies were performed in which

differential interference contrast microscopy and fluorescence microscopy were used to image the PIONs and lipid coating, respectively. These studies also confirmed successful coating of PIONs. We then demonstrated loading PIONs using fluorescently labeled DNA oligomers as a mimic of the siRNA.

Lastly, we characterized uptake of lipid-coated PIONs by primary rat cortical neurons. Spinning disk confocal microscopy was used to image the uptake and localization of PIONs. Our data suggest that the PIONs are efficiently internalized by neurons and are evenly distributed throughout the neuronal soma (primary cell body). Fluorescence associated with the PIONs was also observed in the neuronal processes (axons and dendrites) but to a much lower extent than in the soma.

Significance:

Through the technical work performed on this project, we have significantly advanced the frontiers of science and engineering with respect to our ability to deliver physiological effectors to neurons. Targeted delivery of pharmaceutical agents, including effectors such as siRNA, to the brain is problematic due to issues with crossing the blood-brain-barrier and non-phagocytic nature of neurons in the brain. In this project, we characterized the potential use of porous iron oxide particles as a means of delivering siRNA to temporarily inhibit neurotransmitter function and potentially affect cognitive function associated with diseases such as Parkinson's. This work is potentially of interest to NIH and other agencies concerned with public and military health (e.g., DoD).

Identification and Display of CRLF2 Ligands for Targeted Nanoparticle Delivery to Acute Lymphoblastic Leukemia

158849

Year 1 of 1

Principal Investigator: C. S. Ashley

Project Purpose:

Acute Lymphoblastic Leukemia (ALL) is the leading cause of cancer death in children. Nearly 80% of children diagnosed with ALL survive, but in order to reach that point, they must undergo intense regimens of systemic chemotherapy with numerous short- and long- term side effects. We aim to produce nanoparticles based on virus-like particles (VLPs) of bacteriophage MS2 that specifically target ALL cells for delivery of cytotoxins. We are taking take advantage of the overexpression in high-risk pediatric ALL of the thymic stromal lymphopoietin (TSLP) receptor, CRLF2, by identifying peptide ligands specific for the receptor. Phage display has long been used to identify targeting peptides, but filamentous phage particles themselves make poor drug delivery vehicles. This means that targeting peptides identified by phage display must be chemically synthesized and then conjugated to a more suitable nanocarrier (e.g. liposomes, dendrimers, polymers, etc.). It is well known that changing the structural context in which a peptide was affinity optimized during selection frequently causes it to lose affinity for its receptor. We recently developed a peptide display and affinity selection system based on MS2 VLPs, thus integrating the targeting ligand identification and drug delivery functions into a single particle.

Previous identification of targeting peptides has been accomplished using filamentous phage display. Filamentous phages provide an excellent platform for identifying targeting peptides, but are not suitable as drug delivery vehicles. Until now, it has been necessary to chemically synthesize targeting peptides and conjugate them to an appropriate nanocarrier, a process that requires changing the structural context of the peptide and, therefore, its affinity for the target. Since MS2 VLPs have been recently adapted for peptide display and affinity selection, they can potentially integrate ligand identification and drug delivery functions into a single particle, optimizing the selection, production, and implementation of this technology. The work is performed in collaboration with the University of New Mexico.

Summary of Accomplishments:

Technical accomplishments over the course of this project include:

1. We quantified the binding of particles expressing previously identified ligands to CRLF-2 positive cells using flow cytometry and confirmed that MS2 particles are capable of targeting CRLF-2 positive cells and that the maintenance of peptide conformation is crucial.
2. We analyzed binding of particles to non-model cell systems and identified potential flaws in the current cellular display platform of CRLF-2 for ligand identification.
3. Based on those results, we conducted further VLP-based affinity selection on a better-understood target, Epidermal Growth Factor Receptor (EGFR), and carried out iterative rounds of selections. Through this revised selection process we have identified several families of peptides that potentially bind to EGFR, and we are currently quantifying the fitness of this interaction.
4. We have established several techniques for affinity selection using VLPs and have improved on past protocol strategies for VLP selections. We will apply this knowledge to future CRLF-2 targeting selection protocols.
5. We delivered a featured oral presentation in the "Nanomedicine for Molecular Imaging and Therapy" symposium at the Spring 2012 meeting of the Materials Research Society: "Development

of a Virus-Like Particle Platform for Affinity Selection and Targeted Delivery of Therapeutic Agents to Cancer.” This presentation was featured in the *MRS Meeting Scene* daily highlights.

Significance:

This work directly impacts burgeoning collaborations between Sandia and both the University of New Mexico Cancer Center and MD Anderson Cancer Center and will contribute to the recent emphasis on expanding Sandia’s research repertoire into human-nanoparticle interactions. The research described here will enable future work aimed at developing novel virus-like particles that can selectively target and deliver cargo to pathogenic bacteria and virally-infected cells. Overall, this preliminary work is relevant to several mission areas at Sandia, including Defense Systems and Assessment and Homeland Security and Defense, and will contribute to collaborative proposals to the National Institutes of Health (NIH) and the National Cancer Institute (NCI).

A Cognitive and Economic Decision Theory for Examining Cyber Defense Strategies

161871

Year 1 of 3

Principal Investigator: A. Bier

Project Purpose:

Cyber attacks pose a major threat to modern organizations. Little is known about the social aspects of decision making among organizations that face cyber threats, nor do we have empirically grounded models of the dynamics of cooperative behavior among vulnerable organizations. The effectiveness of cyber defense can likely be enhanced if information and resources are shared among organizations that face similar threats. Cyber defense teams must balance potential benefits from cooperation against motivations not to cooperate, such as potential for embarrassment, group inertia, or competitive strategy. Despite these risks, cooperation could mitigate a range of cyber-related vulnerabilities, including espionage, identity theft, and attacks on critical infrastructure. The purpose of this project is to create a dynamic computational model to address these issues, leading to better scientific understanding of cognitive processes while simultaneously identifying critical gaps and potential improvements in cooperative cyber defense communication and strategy formation.

We are developing a computational model for researching the psychological, social, and economic factors that drive decision making about intra- and inter-group interactions in cyber defense. The model incorporates cultural, cognitive, and institutional constraints and conditions to simulate how cognition and environmental circumstances determine cyber defense strategies and behaviors. The model will serve as a test bed for studying theories of cognition in cyber environments, potentially enhancing scientific knowledge of cognitive processes and improving our ability to model decision making in any context.

If successful, this project will result in the first psychological-socio-economic dynamic model designed for this type of analysis. Validation and uncertainty quantification will bolster confidence and enhance the utility of results. The model will enable better understanding and anticipation of cyber defenders' reactions to organizational strategies and priorities, giving insight into strategic policy design. It will be applicable to any set of organizations, creating flexibility in application while providing useful insight into cognitive processes in cyber defense and cooperation.

Genomic Functionalization: The Next Revolution In Biology

162034

Year 1 of 3

Principal Investigator: P. Imbro

Project Purpose:

Next-generation sequencing technologies have enabled revolutionary advances in areas such as detection and diagnosis of biological agents for human health and biodefense, forensics, and bioenergy. These approaches have also provided an exponential growth in biological data, to the extent that it now costs more to analyze a genome than to sequence it. The principal challenge in analyzing genomic sequence data is predicting the functional significance of most genome subsequences, or genomic functionalization. The knowledge gap between gene sequence and function complicates tasks such as assessing the potential pathogenicity of a biological agent, understanding the health implications of human genomic sequence variations, or understanding how sequence changes may affect the function of enzymes involved in cellulosic biomass deconstruction. This project will develop a genomic functionalization capability at Sandia, which will use operational and functional metadata coupled with a Random Forest machine-learning approach to functionally annotate genomic information from human pathogens. The genomic functionalization machine-learning algorithm will be trained on 30 sequence data sets: 10 human serum samples (provided by SeraCare) and 20 serum datasets submitted to Sandia from the University of California, San Francisco, (UCSF) some of which contain Dengue virus. The performance of the genomic functionalization pipeline will be tested on an additional 70 UCSF Dengue virus-containing serum datasets by comparing its output with the results of “manual” annotation of the data (e.g., biological experts annotating the data by hand).

Self-Deconstructing Algal Biomass as Feedstock for Transportation Fuels

164662

Year 1 of 3

Principal Investigator: R. W. Davis

Project Purpose:

The potential for producing biofuels from algae has generated much excitement based on projections of large oil yields with relatively little land use. However, numerous technical challenges remain for achieving market parity with conventional non-renewable liquid fuel sources. Among these challenges, the energy intensive requirements of traditional cell rupture, lipid extraction, and residuals fractioning of microalgae pose great opportunities for translational research in the nascent field of algal biotechnology. To date, solutions to the aforementioned problems have been sought using technology developed primarily for petrochemical applications. A targeted biological approach to these issues could dramatically reduce both the capital and operating costs of producing fuels from algae. Our novel solution to address these problems is to employ methods of biological engineering to eliminate the need for hardware- and energy-intensive methods for cell rupture, lipid extraction, and residuals fractioning by introducing a triggered cell lysis and enzymatic conversion functionality in a halophilic microalgae suited for mass culture. The output of the proposed enzymatic deconstruction process will consist of a slurry of phase segregated lipidic and aqueous algal metabolites for subsequent transformation to transportation fuels by transesterification, fermentation, and anaerobic digestion.

Until recently, very little progress has been made employing biological engineering for microalgal biofuels applications. However, achievements in genetic analysis and minimally perturbative methods of algal transformation have opened the gates for new research in this area. A prime target for employing biological engineering is the development of biochemically triggered expression of 'deconstruction genes' for decomposing the algal extracellular matrix (ECM). Not only would this process lead to a low-cost lipid extraction process, but also the polysaccharides that compose the ECM will be converted to sugars for fermentation. Our strategy will focus on coupling expression of exogenous mesophilic cellulase and protease enzymes to genes involved in responding to nutrient limitation. This approach will facilitate maximal biomass accumulation prior to deconstruction.

SCIENCE OF EXTREME ENVIRONMENTS INVESTMENT AREA

The Science of Extreme Environments (SEE) investment area seeks to create new knowledge that enables revolutionary advances in the areas of high energy density physics, radiation sciences, pulsed power, and fusion energy for national security needs. A synergistic combination of experiments and theory provides insights into the nature of electronics under exposure to x-rays, gamma rays, neutrons, and other charged particles, and enables the production of high power density x-rays from impressive pulsed power systems. Theoretical computational studies reveal the nature of the complex plasmas formed, and aid in such pursuits as the production of high power microwaves for missile defense. This investment area clarifies scientific understanding about environmental conditions rarely encountered in everyday experience (except, for example, rare situations such as lightning), but which are nevertheless commonplace in several Sandia national security mission areas.

Fundamental Hydrogen Interactions with Beryllium Surfaces: A Magnetic Fusion Perspective Project 148957



Experimental setup for hydrogen-beryllium interaction studies.

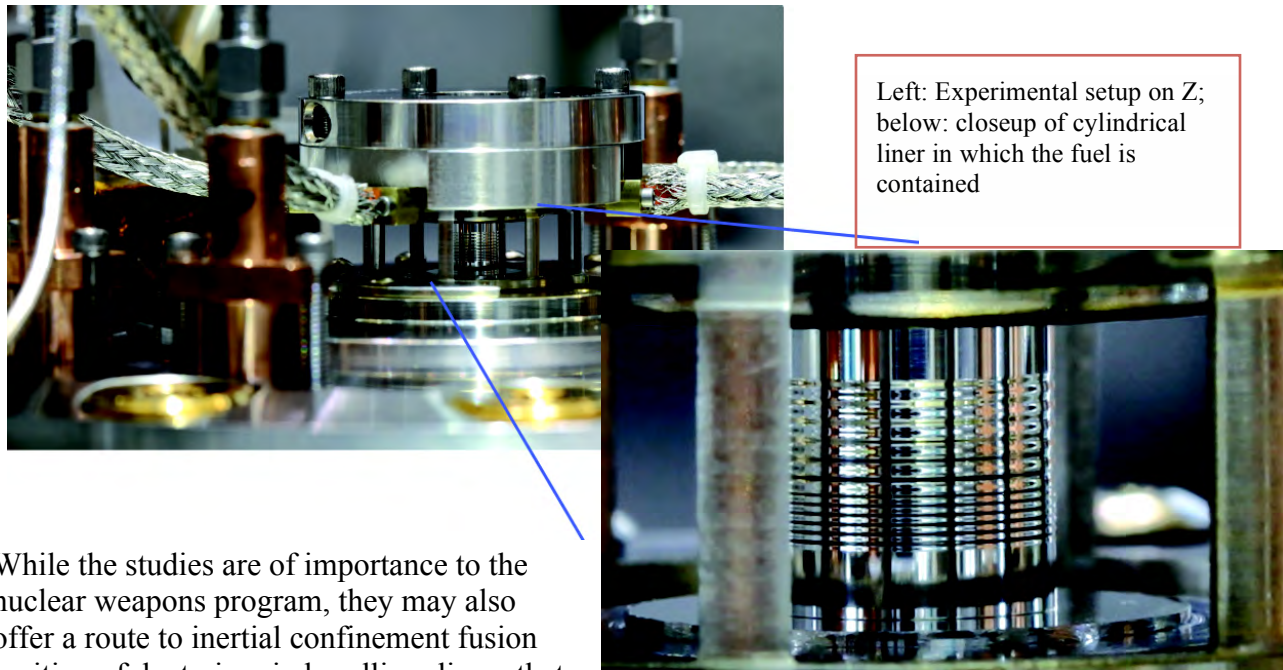
Because beryllium will be the principal material facing deuterium (or deuterium-tritium) plasmas, in reactor vessels for nuclear fusion projects attempting to generate fusion energy — most notably the multinational ITER Project — understanding how it interacts with hydrogen is particularly important to project successes. Hence, this LDRD project studied that interaction using single crystal system to characterize how hydrogen interacts with the beryllium surface. It employed low-energy ion scattering (LEIS) and direct recoil spectroscopy (DRS) to directly detect the configuration of surface-adsorbed hydrogen. These techniques offer much more precise information on hydrogen behavior, and neither has been previously applied to Be(0001)+H.

Using an angle-resolved ion energy spectrometer (ARIES) system, the project obtained “scattering maps” of the Be(0001) crystal that provided insight into how low energy ions are focused along open surface channels. Experiments elucidated the optimal experimental configurations, the results consistent with density functional theory calculations of the hydrogen configuration at low surface coverage.

A key accomplishment was the development of modeling tools to aid in the interpretation of scattering data.

Stability of Fusion Target Concepts on Z Project 141537

This project, recipient of an FY 2011 Defense Programs Award of Excellence, is studying the application of pulsed power from Sandia's Z machine to generate the compression and heating of matter—particularly deuterium fuel—inside magnetized liners of various material.



While the studies are of importance to the nuclear weapons program, they may also offer a route to inertial confinement fusion ignition of deuterium in beryllium liners that could at least reach breakeven energetics, that is, the energy required to achieve ignition of the fuel would be at least equaled by the energy liberated through nuclear fusion (of deuterium nuclei to produce helium plus liberated energy). While this would normally require matter to be compressed and heated to pressures in the range of 100 to 1000 Gigabars, such Magnetized Liner Inertial Fusion (MagLIF), reduces the required pressure to about 10 Gigabars.

The key scientific issue for the MagLIF concept is the stability of the annular cylindrical liner used to compress the fuel. The outer surface of the liner is susceptible to the Magneto-Rayleigh Taylor (MRT) instability, and this project has studied and modeled this phenomenon, at first using aluminum liners, and subsequently fabricating and studying beryllium liners—the recent development of 6 keV backlighting enabling the simultaneous study of the inner and outer surfaces of the imploding liner. This project will advance understanding of fusion plasmas, the stability of z-pinches, and may ultimately be useful for fusion-fission hybrid concepts. During FY 2010-11, the experimental team pursued controlled studies of the stability of liner implosions and the key physics of the overall MagLIF concept and documented this work in a publication. The MagLIF concept was refined using simulations validated by experimental data and a new high-gain fusion target was designed that will increase the utility of this concept, potentially enabling a future fusion power facility.

Science of Extreme Environments Investment Area

Advanced K-Shell X-Ray Sources for Radiation Effects Sciences on Z 141533

Year 3 of 3

Principal Investigator: B. M. Jones

Project Purpose:

The Z machine provides intense 1–10 keV photon energy x-ray environments for radiation effects science (RES) experiments using wire array and gas puff loads. This project seeks to extend the portfolio of x-ray sources available on Z to >10 keV photon energies by exploring a novel load configuration. This project is allowing us to explore the parameter space of these loads and assess their applicability to x-ray generation.

Summary of Accomplishments:

Several novel x-ray source target designs have been studied during the course of this project. In the final week of experiments, we obtained very exciting results producing record laboratory yields of >10 keV photons and an excellent data set that will help in the understanding of the physics of these sources. These results are likely to feed back on other experimental campaigns at Z, and we have already demonstrated that they will enable unique radiation effects experiments. A particular emphasis of this project is to use numerical modeling to design the experiments, and then test the models using measured data. During this project, we have had an excellent relationship between modeling and experimentation, with experiments suggesting modifications to numerical designs and vice versa. The High Energy Density Council has approved a week of experiments in calendar 2013 continuing the source development that was initiated by this project.

Significance:

This work is relevant to DOE strategic needs in nuclear weapons stewardship (providing higher photon energy sources for RES work on Z), and improves the capacity of existing facilities for more sophisticated scientific research (basic physics of pulsed-power-driven x-ray sources).

High Pulse Energy Fiber Laser Sources 141534

Year 3 of 3

Principal Investigator: R. Bambha

Project Purpose:

High-performance lasers can perform critical tasks in areas such as intelligence, surveillance and reconnaissance, but suitable lasers have typically been very unwieldy. Compact lasers capable of producing multi-mJ pulses with diffraction-limited beams and low nonlinearities are desirable but not currently available. Current laser systems employing bulk amplifiers are inherently large and typically require multiple stages of amplification, which increases cost, size, and complexity. This project has demonstrated a path to lasers that can achieve all the desired optical properties simultaneously in a compact size by leveraging recently developed phosphate glass fibers with very high rare-earth (RE) doping concentration. Phosphate glass can accommodate RE doping levels approximately 20 times higher than conventional fused silica. This feature enables high-gain, single-stage, mJ-level amplifiers with short lengths (~10 centimeters), which nearly eliminates the nonlinear effects that limit energies and broaden spectral widths in conventional fused-silica fibers. Our approach is expected to reduce cost, size, and weight of the system while preserving diffraction-limited beam quality. Furthermore, phosphate glass has a large amplification bandwidth, offering wideband pulse amplification.

The purpose of this project was to create fiber amplifiers that surpass the performance of previous fused silica fiber amplifiers using phosphate glass. In order to achieve this, we developed new methods for tapering soft-glass fibers to produce diffraction-limited output.

Summary of Accomplishments:

Through this effort, Sandia attained a unique knowledge base for building pulsed phosphate glass fiber amplifiers. We also developed new capabilities for building amplifiers in the 2-micron wavelength region, which affords particular benefits for operations and eye safety.

We made significant progress in pulse energy, thermal management, glass characterization, amplifier modeling and 2-micron seed laser development. We demonstrated 2.25 mJ output at 1-micron wavelength from a 5%-doped Yb:phosphate fiber amplifier with a 49-micron core diameter producing a multimode output beam. We developed methods for tapering and mode-matching fibers to maintain diffraction-limited beam quality using 35-micron core fiber, which attained 0.7 mJ single-mode output. The limit to the attainable energy in all our work was optical damage resulting from the unsuitably short pulse durations of the seed lasers we used. We performed damage threshold measurements on phosphate and silicate glasses using a focused Gaussian beam, and we also measured the damage level for fused silica for comparison. From these measurements, we found the damage level for phosphate glass to be slightly less than fused silica (approximately 20% lower) and approximately 40% higher than silicate glass. Using these results, we have determined that the pulse duration for maximum energy should be greater than 50 ns for single-mode multi-mJ output.

We developed a dynamic fiber-amplifier model and a numerical simulator that is temporally, spectrally, and spatially resolved, allowing control of amplifier parameters and seed pulse characteristics. The model compares well with published results and the simulator runs under Matlab using available parallel processing capability. We also developed a seed source for the 2-micron wavelength region using Tm and Tm-Ho co-doped fibers addressing the shortcomings we encountered with our 1-micron seed lasers. We demonstrated single-frequency, long-duration pulse generation that will be well suited for use with the large-core short fiber techniques applied to the 2-micron region.

Significance:

This project demonstrated multi-mJ output from novel, short, highly doped, large-core fiber amplifiers. The glass properties along with short length and large core of the fibers combine to permit amplifiers capable of low distortion for either large-bandwidth or single-frequency amplification. Such amplifiers are ideal for master oscillator power amplifier systems with aggressive spectral requirements that would be entirely unattainable using conventional fused silica fiber. A wide range of applications of interest to agencies such as DHS—can be enabled by this technology including those requiring very high range resolution and very narrow detection bandwidth.

Mixed Hostile-Relevant Radiation Capability for Assessing Semiconductor Device Performance

141535

Year 3 of 3

Principal Investigator: E. S. Bielejec

Project Purpose:

Exploring the combined effects of high dose-rate ionizing radiation and displacement damage is critically important to understanding the response of semiconductor devices to hostile radiation environments. Existing radiation test facilities cannot probe the combined effects without extraneous background radiation. To provide a tool for detailed studies of the mechanisms that affect semiconductor device response, we propose combining ionizing irradiation, produced by pulsed electron and laser irradiations, with displacement damage, introduced by pulsed high energy silicon ions, to create a high-fidelity simulator of the radiation threat environment. The ability to independently control both the magnitude and timing of ionization and displacement damage will permit a) simulation of unique neutron-gamma radiation exposures, b) exploration of synergistic effects, and c) confirmation of device physics models in previously inaccessible regimes. Controlled time-dependent ionization will also explore device responses to a range of stockpile to target scenarios. By using both electron and laser irradiations to introduce ionization to a device, oxide and bulk ionization effects will be independently characterized for Si devices. A fundamental aspect of this program is research into the unexplored synergistic effects of displacement damage and ionizing radiation. Our goal is to develop a mixed radiation exposure capability that can be used to confirm our understanding of the underlying physics of these unique radiation environments and to evaluate the effects that may arise in new device designs or materials considered for insertion into the stockpile.

Summary of Accomplishments:

We explored a range of synergistic effects combining high dose rate ionization with displacement damage on Si bipolar junction transistors. We demonstrated an effective change in the early time gain of the devices that was as large as 2–3x. This improvement of the device gain at early-times under combined ionization and displacement damage was attributed to an enhanced photocurrent driven annealing of the Si devices. We explored the dose rate dependence and the timing between the ionization and the displacement damage irradiations. In addition, we demonstrated the ability to provide a high fidelity physical simulator of the radiation threat environments using a combination of short pulse electron irradiation (<10 ns) to simulate the prompt gamma environment, a mid-length lower dose rate sustained gamma pulse by laser irradiation and a later time heavy ion irradiation to simulate the neutron damage. In sum, we explored a range of synergistic effects and demonstrated the physical capability to provide a high fidelity physical simulator of the radiation threat environments.

Significance:

Over the course of FY 2012, we have demonstrated an ability of our low energy pulsed electron gun system to delivery <10 ns pulses on target with dose rates as large as $\sim 10^{12}$ rads(Si)/s. This is a critical milestone in our ability to directly provide a high-fidelity physical simulation of a variety of potential radiation threat environments. This work lays the foundation for the continued development of a physical simulator of the hostile-relevant neutron-gamma environment by generating the prompt gamma, sustain gamma, and neutron environments necessary. These results have the potential to directly impact Sandia's continuing nuclear weapons (NW) qualification work.

Stability of Fusion Target Concepts on Z 141537

Year 3 of 3

Principal Investigator: D. B. Sinars

Project Purpose:

Achieving inertial confinement fusion ignition in the laboratory requires matter to be compressed and heated to pressures in the range of 100 to 1000 Gigabars. Pulsed power drivers offer efficient, inexpensive ways to heat and compress matter, but it is not yet known if they can reach the tremendous pressures needed for fusion ignition. A new concept, Magnetized Liner Inertial Fusion (MagLIF) (S.A. Slutz et al., 17, 056303 [2010]), reduces the required pressure to about 10 Gigabars by magnetizing and preheating the fusion fuel. Modeling suggests that this concept could lead to scientific breakeven on Z (fusion energy comparable to energy delivered to the fuel).

The key scientific issue for the MagLIF concept is the stability of the annular cylindrical liner used to compress the fuel. In particular, the outer surface of the liner is susceptible to the Magneto-Rayleigh Taylor (MRT) instability, which may be enhanced by an electrothermal instability. At present there are no stability studies of liner implosions with drive pressures greatly exceeding the strength of materials, as would be the case for MagLIF. With the recent development of 6 keV backlighting and the ability to fabricate beryllium liners, the Z facility provides a unique venue to simultaneously study the inner and outer surfaces of the imploding liner. This will be critical to determining the liner integrity during the implosion. The goal of this project has been to understand the stability of cylindrical implosion systems relevant to the MagLIF concept.

This project has studied a new, high-risk fusion concept that will advance our understanding of fusion plasmas, the stability of z-pinchs, and which may ultimately be useful for fusion-fission hybrid concepts. The concept is not a high-gain system, which has been the traditional focus of the existing sponsored inertial confinement fusion program.

Summary of Accomplishments:

This project supported the execution and analysis of thirty-five liner implosion experiments on the Z pulsed power facility. These experiments are providing key benchmarking data for validating the predictions of simulations, a fact recognized by the broader community in the form of several invited talks and high-profile publications. In most cases, we are eventually able to obtain good agreement between the simulations and the data, but the level of agreement is sensitive to how the initial liner conditions are treated. Much of the work was conducted in the specific context of a new MagLIF concept. However, the liner stability data is fundamental to all magnetically driven systems. This project also supported continued development and modeling of the MagLIF concept, including the development of a high-yield, high-gain variant. Finally, the project succeeded in developing and demonstrating magnetic field coils capable of creating 10 T axial magnetic fields over a large volume. The capacitor banks and other infrastructure needed to field these coils on the Z facility are presently being installed. These field coils are needed both to test the MagLIF concept by allowing us to magnetize the fusion fuel, and also to investigate whether liner implosions can be stabilized using magnetic fields. While our work was conducted in the specific context of MagLIF, the idea of magnetizing and preheating the fuel to relax the requirements for fusion can be applied to other inertial confinement fusion platforms (e.g., radiation-driven spherical capsule implosions.)

Significance:

This project advanced our progress toward demonstrating a new fusion concept. In this concept, a cylindrical liner implosion compresses magnetized and preheated fuel to the conditions needed for fusion. A key scientific issue for magnetically driven systems is the stability of the liner, which is susceptible to the magneto-Rayleigh-Taylor instability. This instability can disrupt the liner implosion and prevent it from successfully compressing and confining the fuel. The liner stability data collected by us is fundamental to all magnetically driven systems, and the idea of magnetizing and preheating fuel to relax requirements can be applied to any inertial confinement fusion (ICF) system. This concept is an active area of interest for DOE/EERE (Energy Efficiency and Renewable Energy) as one of the initiatives to discover and develop renewable, low-carbon energy sources.

Refereed Communications:

R.W. Lemke, M.R. Martin, R.D. McBride, J.-P. Davis, M.D. Knudson, D.B. Sinars, I.C. Smith, M. Savage, W.A. Stygar, K. Killebrew, D.G. Flicker, and M.C. Herrmann, "Determination of Pressure and Density of Shocklessly Compressed Beryllium from X-Ray Radiography of a Magnetically Driven Cylindrical Liner Implosion," in *Proceedings of the American Institute of Physics Conference*, pp. 473-476, 2012.

M.R. Martin, R.W. Lemke, R.D. McBride, J.-P. Davis, and M.D. Knudson, "Analysis of Cylindrical Ramp Compression Experiment with Radiography Based Surface Fitting Method," in *Proceedings of the American Institute of Physics Conference*, pp. 357-360, 2012.

M.R. Martin, R.W. Lemke, R.D. McBride, J.-P. Davis, D.H. Dolan, M.D. Knudson, K.R. Cochrane, D.B. Sinars, I.C. Smith, M. Savage, W.A. Stygar, K. Killebrew, D.G. Flicker, and M.C. Herrmann, "Solid Liner Implosions on Z for Producing Multi-Megabar, Shockless Compressions," *Physics of Plasmas*, vol. 19, p. 056310, 2012.

S.A. Slutz and R.A. Vesey, "High-Gain Magnetized Inertial Fusion," *Physical Review Letters*, vol. 108, p. 025003, January 2012.

R.D. McBride, S.A. Slutz, C.A. Jennings, D.B. Sinars, M.E. Cuneo, M.C. Herrmann, R.W. Lemke, M.R. Martin, R.A. Vesey, K.J. Peterson, A.B. Sefkow, C. Nakhleh, B.E. Blue, K. Killebrew, D. Schroen, T.J. Rogers, A. Laspe, M.R. Lopez, I.C. Smith, B.W. Atherton, M. Savage, W.A. Stygar, and J.L. Porter, "Penetrating Radiography of Imploding and Stagnating Beryllium Liners on the Z Accelerator," to be published in *Physical Review Letters*.

Ultrashort Pulse Laser-Triggering of Long Gap High-Voltage Switches 141538

Year 3 of 3

Principal Investigator: P. K. Rambo

Project Purpose:

Long-gap, laser-triggered, high-voltage discharges have numerous applications from super-radiant laser sources and laser wakefield acceleration to laser-triggered spark gaps used for megavolt switching in pulsed power devices to triggered and guided lightning. The problem facing all such efforts is the ability to create long ionized channels with adjustable plasma density and extended plasma lifetimes in order to improve discharge reliability, reduce temporal jitter, and allow for longer gaps and higher hold-off voltages. To overcome these problems, we are using sub-picosecond laser pulses to examine switching aspects in long-gap high-voltage discharges, with special emphasis on extension of plasma lifetime. Prior application of such ultrashort pulse (USP) lasers (instead of the nanosecond pulses more commonly used in pulsed power switching) in state-of-the-art high-voltage switching has focused on different parts of the problem, demonstrating very low jitters with USP lasers but at low voltages or demonstrating high-voltage discharges with USP lasers but with no attention to jitter.

The proposed work innovates upon the current state-of-the-art by joining aspects of various former efforts while directly addressing the key issue of improvements in laser plasma density, length, and lifetime. Such advances occur by considering multiple USP and nanosecond laser pulses for the plasma improvements. To do this, complex ionization and recombination dynamics must be properly understood, requiring a systematic study of relevant gas ionization. Subsequent to this study, we are improving ionization and increasing the plasma lifetime using methods such as multiple USPs and additional long pulse heating beams. With sufficiently spatiotemporally improved plasmas, we can leverage unique expertise in pulsed power, lasers, and complex modeling to maximize long-gap switching by these USPs. The novel realization of these improvements will yield switches with higher voltage operating points and lower jitters, features desired in future generation pulsed power machines.

Summary of Accomplishments:

Efforts to quantify gas ionization with respect to laser intensity were complicated by the convolution of nonlinear Kerr self-focusing and plasma defocusing. Subsequently, we developed a novel approach of using wavefront curvature change to measure nonlinear focal shift. This system allowed validation of the Perelomov, Popov, Terent'ev (PPT) model of multiphoton ionization at atmospheric pressure, which, to our knowledge, had not been achieved previously.

Several techniques for extending plasma spatial extent and lifetime were explored. Plasma lengths were extended via the concatenation of the ionized channels created by multiple laser pulses. The method involved generating a 2-pulse sequence wherein the wavefront of one pulse is changed (for example, by Kerr effect, a separate telescope, or chromatic aberration) such that, upon focus with a common lens, the pulses focus in different spatial locations. Multiple pulses were also used to increase lifetime via re-ionization and plasma heating.

A high voltage (100 kV DC) switch in air was developed, commensurate with laboratory and safety constraints. Nanosecond switch testing indicated that specific switch parameters could be optimized by tailoring the laser plasma that initiates switching. For example, for a given laser energy/focal optic under fixed high voltage and gap, the switch runtimes were optimal for the laser plasma near mid-gap with the focal lens at normal incidence. Twisting the lens to 5 degrees extends the plasma slightly, marginally increasing runtimes while reducing jitter by a factor of 2.

Modeling efforts have approached the laser-triggered switch from the perspectives of laser ionization and streamer development/switch closure. A laser ionization model has been developed which accounts for diffraction, multiphoton ionization, plasma defocus, cascade ionization, self-focusing, plasma recombination, and group velocity dispersion. Additionally, a fully 3D model has been developed of streamer evolution in sulfur hexafluoride switching gas. Simulated switch closures and runtimes compare well to experimental data.

Significance:

Low-jitter high-voltage switches are used in a variety of areas central to DOE efforts: Pockels cell drivers for lasers, pulsed power science, accelerators, and explosives triggers. In addition, guided, long-gap, laser-triggered, high-voltage discharges have been of historical interest to directed energy advocates in their missions.

Modeling efforts can now simulate the behavior of laser-triggered switches reasonably well. This capability allows better failure mode analysis and continuous improvement on existing systems while giving future switch designs a better chance of success.

X-Ray Thomson Scattering Measurements of Warm Dense Matter

141540

Year 3 of 3

Principal Investigator: J. E. Bailey

Project Purpose:

Warm dense matter exists at the boundary between condensed matter and plasma physics and challenges theoretical understanding. It is also critical for applications, including z-pinch and inertial fusion laboratory experiments and in astrophysical objects such as white dwarfs and giant planets. Modern high energy density facilities have made it possible to create warm dense conditions in the laboratory. Generating warm dense conditions is challenging in and of itself, but thorough understanding also requires accurate detailed diagnostics. This project is advancing warm dense matter physics by combining x-ray Thomson scattering, a powerful diagnostic for warm dense matter, with extreme environments created at the Sandia Z facility. X-ray Thomson scattering (XRTS) uses an intense laser (in this case Z Beamlet) to produce quasi-monochromatic x-rays that probe matter at high density. Measurements of the spectrally resolved, scattered x-rays determine both temperature and density. We are developing a flexible capability suitable for diagnosing either shock- or radiation-heated samples. The capability will be exploited to advance cutting edge physics topics selected from candidates such as warm dense matter equation of state, influence of correlations on atoms in dense matter, and white dwarf envelopes.

Summary of Accomplishments:

The foundation for the new XRTS capability on Z has been established, which will help maintain Sandia's leadership in dynamic materials and radiation science. Specific achievements include the following:

1. A theoretical framework suitable for designing and interpreting Z-XRTS experiments has been developed in-house at Sandia. The new theoretical code, based on quantum mechanical approaches that treat scattering from bound and free electrons on an equal footing, goes beyond previous scattering calculations that use a chemical picture of the atoms.
2. The magnetohydrodynamics code Arbitrary-Lagrangian-Eulerian General Research Applications (ALEGRA) was used to simulate the expected warm dense matter (WDM) states created by Z in the scattering experiments.
3. A new high-sensitivity x-ray scattering spherical spectrometer (XRS3) was designed and fabricated. The XRS3 spectrometer will enable benchmark quality data because it will measure x-ray scattered signals with both high-spatial ($\sim 75 \mu\text{m}$) and -spectral ($E/\Delta E \sim 1500$) resolution. The quality of several types of spherically bent crystals was investigated using the Manson x-ray source.
4. Experiments were performed on the Z Beamlet laser (ZBL) facility to develop an x-ray source for Z-XRTS experiments. In addition, x-ray scattering from ambient CH₂ foam was measured, demonstrating the simultaneous measurement of source and scattered x-rays.
5. Preparations for upcoming Z-XRTS experiments were completed. Because it will be the first time that ZBL will be focused on-axis of Z with a Z-digital motion processor (DMP) load, debris mitigation plans were developed to protect the final optical assembly of ZBL.
6. The initial set of Z-XRTS experiments will demonstrate the capability of x-ray scattering as a much needed temperature diagnostic for opaque WDM samples. The main experimental goal will be to obtain high-quality temperature data that will benchmark equation-of-state (EOS) models.

Significance:

The initial set of Z-XRTS experiments will demonstrate the capability of x-ray scattering as a much needed temperature diagnostic for opaque WDM samples. Specifically, the temperature measurement from elastic x-ray scattering of shocked single crystal lithium deuteride will allow EOS completion of a material of high interest. Such measurements can fill a critical gap in Sandia's dynamic materials research and will thus benefit the DOE dynamic materials and weapons missions. This is just one of many topics that represent vastly improved ability to characterize materials in WDM and extreme plasma conditions. This research impacts DOE missions in dynamic materials and stockpile stewardship. In the longer term x-ray scattering can also provide insight into inertial fusion plasma properties and, thus, impact the pursuit of carbon-neutral energy

Laser-Based Radiation-Induced Conductivity in Kapton Polyimide Dielectrics at High Dose Rates

148196

Year 3 of 3

Principal Investigator: M. L. McLain

Project Purpose:

The presence of radiation-induced conductivity (RIC) in Kapton polyimide and other dielectric films can have important consequences for electrical components exposed to radiation environments. Previous studies using a linear accelerator (LINAC) to produce high-energy electron beam exposures at dose rates up to 10^{10} rad/s have indicated that the prompt RIC response has a nonlinear, power-law dependence on dose rate. For dose rates above 10^{10} rad/s, it is assumed that the RIC response also has a power-law dependence on dose rate based on lower dose-rate data. However, it has been difficult to confirm these findings with current flash x-ray or LINAC test facilities. Determining the RIC response characteristics of Kapton and other dielectric materials for higher dose-rate exposures will, therefore, require the development of innovative testing techniques in order to validate model predictions based on lower dose-rate data.

In this project, the feasibility of using high-intensity, short-duration laser pulses to obtain high dose-rate RIC data on Kapton polyimide dielectrics is being evaluated. This is accomplished via single-pulse shots from a Q-switched Nd:YAG laser with a wavelength of 532 nm, a full width half max of 2 ns, a beam diameter of 5 mm, and a variable energy range. First-order calculations indicate that dose rates greater than 10^{10} rad(Si)/s can be attained in Kapton with this pulsed laser system. The results will ultimately be applied to advanced models for RIC that currently lack high dose-rate experimental validation data. This approach has cutting-edge character and novelty in that such a method has not been considered for the acquisition of RIC data. Moreover, it appears that a focused study of the photoconductive properties of Kapton as a function of dose rate has not been described in any scientific publication. A key S&T challenge addressed in this project will be the acquisition of radiation effects data without the use of previous testing capabilities.

Summary of Accomplishments:

This project has been the first experimental demonstration of the laser-based technique being used to obtain RIC data on Kapton polyimide or any other dielectric. Previous studies on Kapton suggested that multiple laser pulses were needed to see an increase in the photoconductivity. In the experiments, two different types of Kapton RIC cells were fabricated. The first design had an indium tin oxide (ITO) front electrode and the second design had a “cross-hatch” aluminum front electrode (i.e., had areas without aluminum to allow laser penetration into the underlying Kapton). In the initial experiments, we discovered that the output current for the ITO RIC cell exhibited a long relaxation time (i.e., capacitive tail) after the laser pulse ended. Therefore, the “cross-hatch” design was chosen to investigate the laser-based Kapton RIC response.

After analyzing the results, we found that the laser-based RIC is linearly dependent on the applied bias and varies as a power of the laser energy and dose rate. The slope of the fit from the RIC vs. laser energy plot (or dose rate) was two. A slope of two is indicative of a two-photon absorption or trap-assisted excitation process. In the future, we plan to conduct experiments with a lower wavelength laser. If the wavelength of the laser is below the transmission edge, electron-hole pairs should be created through a single photon absorption process. This will result in larger RIC signals due to increased quantum efficiencies and allow for a better correlation to previous RIC data.

We constructed a Kapton calorimeter to correlate the laser pulse energy to an effective dose rate in Kapton. The calorimeter results were confirmed with energy absorption measurements.

Significance:

The ability to obtain accurate radiation-induced conductivity (RIC) data for model development and validation at high dose rates has been difficult, if not impossible, with current experimental techniques. This is mainly due to rising costs, dwindling test facilities, and the fidelity of the RIC data obtained at the available facilities. In this project, we had the first experimental demonstration of the laser-based technique. It was shown that high dose-rate laser-based RIC measurements on Kapton are viable, but still exploratory. Radiation-induced conductivity data on Kapton and other pertinent dielectrics are vital to existing models of cable SGEMP. By expanding and improving the laser-based technique, this project will have a direct impact on the DOE-NNSA mission of stockpile stewardship. There is also strong potential interest from satellite hardening programs and select other DoD systems (e.g. missile interceptors for MDA).

Refereed Communications:

M. McLain, E.F. Hartman, H.P. Hjalmarson, and G.R. Chantler, "Laser-Based Radiation-Induced Conductivity in Kapton Polyimide Dielectrics at High Dose Rates," in *Proceedings of HEART Conference*, 2012.

M. McLain, E.F. Hartman, H.P. Hjalmarson, and G.R. Chantler, "Laser-Based Radiation-Induced Conductivity in Kapton Polyimide Dielectrics at High Dose Rates," to be published in *Journal of Radiation Effects, Research and Engineering*.

Fundamental Hydrogen Interactions with Beryllium Surfaces: A Magnetic Fusion Perspective

148957

Year 3 of 3

Principal Investigator: R. Kolasinski

Project Purpose:

Once completed, the magnetic fusion reactor (ITER), a multinational partnership, will demonstrate for the first time, controlled ignition and extended burn of deuterium-tritium plasmas. Because beryllium will be the principal plasma-facing material in the reactor, understanding how it interacts with hydrogen is particularly important. There has been a strong desire to understand hydrogen recycling, implantation, diffusion, and recombination from beryllium surfaces from a fundamental, atomic-scale perspective using first-principles modeling techniques. Examining how hydrogen binds and interacts with basic single crystal systems is an ideal way to validate model predictions. The Be(0001)+H system is particularly interesting because it is an example of a low-index, low-Z system which has been sparsely studied. While reconstructions of Be(0001) induced by H adsorption have been examined using electron diffraction and spectroscopy techniques, such methods do not provide direct sensitivity to the adsorbate configuration. We are using low energy ion scattering (LEIS) and direct recoil spectroscopy (DRS) to directly detect the configuration of surface-adsorbed hydrogen. These techniques offer much more precise information on hydrogen behavior, and neither has been previously applied to Be(0001)+H. In addition, our LEIS instrument at Sandia/California has been uniquely optimized for hydrogen detection, and we have developed a number of innovative techniques to study H adsorption on single crystals [Kolasinski, *Phys. Rev. B* 2009]. Such methods will also enable us to characterize the exchange between different gas species on surfaces, achieved by heating the sample and monitoring the scattering/recoil intensity from H and D. For more detailed information on the bonding between the H and Be atoms, we propose to use time-of-flight techniques. Taken together, these measurements offer value from a basic surface science perspective and will strengthen Sandia's expertise in the Be+H system within the fusion community.

Summary of Accomplishments:

In FY 2012, we obtained the first scattering measurements from the Be(0001)+H(ads) system with our angle-resolved ion energy spectrometer (ARIES) system. We obtained "scattering maps" of the Be(0001) crystal that verified the surface structure and provided insight into how low energy ions are focused along open surface channels. A key technical challenge addressed was the ability to directly detect hydrogen on beryllium surfaces, in addition to ensuring that a clean surface can be readily maintained when dosing with atomic hydrogen. Our initial experiments elucidated the optimal experimental configurations. Dosing the sample with atomic hydrogen produced a distinct recoil signal that was consistent with hydrogen residing three-fold hollow sites on the surface. This result is consistent with density functional theory (DFT) calculations of the hydrogen configuration at low surface coverage.

A key accomplishment of this project has been the development of modeling tools to aid in the interpretation of scattering data. The theoretical framework needed to interpret LEIS experiments is still rudimentary. However, by applying novel molecular dynamics techniques to the problem, we were able to make considerable advances to how low energy scattering is modeled, especially at grazing incidence. These results appear in a recent article published in *Physical Review B* and have led to a proposal submitted to DOE.

We also developed a unique time-of-flight experimental detection capability for our ARIES instrument. As the name implies, this system involves measuring ion flight times to determine ion energies. This type of detector is sensitive to both ions and neutral particles, thereby removing a key uncertainty from modeling the experimental data. In addition, it reduces the dose required to obtain a measurement by a factor of 10^4 compared with more conventional detection techniques. With this new diagnostic, we were able to perform much more detailed surface structure measurements than was previously possible.

Significance:

Ensuring that plasma-facing materials can withstand the high particle fluxes encountered in magnetic fusion devices is a pressing technological challenge in magnetic fusion research. Our FY 2012 work enhanced the underlying science needed to model how hydrogen-beryllium interactions, a key priority for the DOE fusion energy science program. In addition, we anticipate many benefits to the broader S&T community. The models developed with this project advance the state-of-the-art for ion scattering and direct recoil spectroscopy simulations, two widely used surface analysis techniques. From these perspectives, this work therefore contributes DOE's mission of basic scientific discovery.

Refereed Communications:

R.D. Kolasinski, N.C. Bartelt, J.A. Whaley, and T.E. Felter, "Channeling of Low Energy Ions on Hydrogen-Covered Surfaces," *Physical Review B*, vol. 85, p. 115422, March 2012.

Low Energy Electron-Photon Transport 151362

Year 2 of 3

Principal Investigator: R. P. Kensek

Project Purpose:

Radiation transport codes are limited by the accuracy of the physics models. General-purpose codes make use of tabulated independent-atom models for the cross sections which are either only evaluated down to about one kilo-electron-volt or extend further with acknowledged large errors (estimated as 1000 percent in solids at the lowest energies). The paradigm shift we propose is to generate what would have been tabulated atomic cross sections, but to also include molecular (coherent scattering) and/or solid-state effects for each material specified. The challenge of this approach is to include these materials properties for each relevant interaction cross section through a reliable numerical technique.

Interest in such a capability is motivated by applications involving low-energy electron and/or photon transport such as transport through nanostructures, understanding experiments from x-ray sources such as Sandia's Z-machine, and better understanding of the energy-resolution limitations of gamma detectors due to secondary-electron emission.

The paradigm shift involves generating elemental cross sections for each material, incorporating materials effects (in particular molecular coherent scattering and solid-state effects) as they uniquely affect each element in that particular material. This involves identifying a reliable technique for each change for each relevant electron and photon interaction, which can be accomplished for a general-purpose radiation transport code.

Modeling Electron Transport in the Presence of Electric and Magnetic Fields 151363

Year 2 of 3

Principal Investigator: W. C. Fan

Project Purpose:

Strategic weapon systems must be able to survive the hostile radiation environment produced by nuclear detonations. For example, a potentially large System Generated Electromagnetic Pulse impinges on electrical or electronic components. Existing modeling/simulation tools assume that electron transport is totally independent from the fields created by the deposited charges, an assumption that becomes invalid if the low-energy electrons are considered.

A related problem is spacecraft charging due to the accumulation of low-energy electrons on the outside surface of a satellite, which can cause electrical arcing, breakdown of dielectrics, and eventually lead to the destruction of electronics and failure of mission capability. Current methods for charging predictions oversimplify the relevant physics, such as the dynamic interaction between incident electrons and electric fields generated by deposited charge. With frequent buildup of potentials on the order of 10 kV on spacecraft surfaces, the effect of the high-flux, trapped electrons in the 1-100 keV range could be significant. Current models give rough predictions, but large safety margins are required due to significant uncertainty.

This project is addressing these issues through model development and numerical simulation, by creating new deterministic algorithms and implementations for multi-dimensional electron transport in materials in the presence of electric and magnetic fields.

Mesoscale Modeling of Dynamic Loading of Heterogeneous Materials 151364

Year 2 of 3

Principal Investigator: J. Robbins

Project Purpose:

Material response to dynamic loading is often dominated by microstructure (grain structure, porosity, inclusions, defects). An example critically important to Sandia's mission is dynamic strength of polycrystalline metals where heterogeneities lead to localization of deformation and loss of shear strength. Microstructural effects are of broad importance to the scientific community and several institutions within DoD and DOE; however, current models rely on inaccurate assumptions about mechanisms at the subcontinuum or mesoscale. Consequently, there is a critical need for accurate and robust methods for modeling heterogeneous material response at lower length scales.

A mesoscale modeling capability would serve two essential roles. The first is to simulate in full detail the response of polycrystalline material to dynamic loading. In this case, the microstructural details appear explicitly in the simulation. This approach is computationally expensive (days on a supercomputer), but provides direct insight into the microstructural origins of material response. The second role, with potentially broader impact, is to inform lightweight (minutes on a desktop computer) continuum models with information from mesoscale simulations. At longer length scales, where Direct Numerical Simulation (DNS) of microstructural effects is not computationally feasible, "upscaling" techniques are a proven approach. Unfortunately, these methods typically assume static equilibrium, making them inappropriate for our applications. Further, current upscaling methods do not leverage statistical information about material response made available through mesoscale calculations. This project will address these problems using Sandia's unique computational capabilities and codes to perform DNS of a statistically significant number of microstructure realizations. Results will inform development of much needed dynamic upscaling models.

Material strength has a high priority in the dynamic materials program, and yet, our understanding of the fundamental processes is relatively poor. Significantly, experimentally measured dynamic strength differs substantially from what simple continuum models predict largely due to microstructural effects. We are developing advanced models that account for mesoscale effects on dynamic strength.

Dynamic Temperature Measurements with Embedded Optical Sensors 151365

Year 2 of 3

Principal Investigator: D. H. Dolan, III

Project Purpose:

Dynamic compression experiments provide unique insight into material behavior under extreme conditions. To fully utilize these experiments in equation of state and phase diagram studies, temperature measurements are needed in the compressed state. Despite years of effort, dynamic temperature measurements are generally considered unreliable. This skepticism is largely due to problems with optical pyrometry. Time-resolved pyrometry measurements are technologically difficult, particularly at the modest temperatures (<1000 K) characteristic of ramp wave compression. Pyrometry also requires information about sample emissivity, a property that typically varies during dynamic compression.

Existing alternatives to pyrometry are useful in certain settings, but not for general temperature measurements. Stokes/anti-Stokes Raman spectroscopy, for example, is extremely material-specific and is not useful for studying the temperature of metals. Neutron resonance spectroscopy can be used to probe temperature in metals, but special facilities are required to generate sufficient neutron flux. Embedded electrical gauges (thermocouples and thermistors) show some promise, but are difficult to use in conductive samples or pulsed power environments.

The goal of this project is to develop optical gauges for dynamic temperature measurements, particularly during ramp wave compression. The use of an embedded gauge anchors the measurement to the properties of standard material, rather than the various samples of interest. At the same time, optical coupling avoids the electrical difficulties of embedded thermocouples/thermistors. To be useful in dynamic compression research, the gauges must show measurable changes in the visible spectrum (400-700 nm) on nanosecond time scales. The gauges must be very thin (<0.001 mm) for rapid thermal equilibration with the sample, yet not so thin as to be transparent to the diagnostic. At this juncture, gold reflectivity has been identified as the most promising temperature gauge for this project, though other metals (notably copper and silver) may also be pursued.

Spectral Line-Broadening in White Dwarf Photospheres

151366

Year 2 of 3

Principal Investigator: G. A. Rochau

Project Purpose:

White Dwarf (WD) stars are potentially the most accurate independent chronometers for constraining the ages of the Galactic disk, halo, and star clusters, and provide a lower limit to the age of the universe. This accuracy depends on stellar evolution models benchmarked against observational data on WD properties: mass and surface temperature. The primary method to determine these properties is through comparison of observed optical line profiles to synthetic spectra from theoretical atmosphere models, adjusting the assumed mass and temperature to obtain the best fit. Understanding the line profiles and how they relate to the plasma conditions is critical to the precise and accurate determination of the WD properties and their inferred ages. The stellar masses inferred from this spectroscopic method, however, disagree with recent gravitational redshift measurements. In addition, the spectral analysis breaks down completely at low surface temperatures. Inaccuracy in the line-shape theory is the leading hypothesis for this breakdown at plasma conditions that span $T_e = 0.3\text{--}5\text{ eV}$ and $n_e = 10^{(16\text{--}18)}\text{ cm}^{-3}$. We are engaged in testing the line-shape theory by accurately measuring the emergent line profiles from well-characterized hydrogen plasmas heated to WD conditions by the $\sim 1\text{ MJ}$ of x-rays produced on the Z machine. Testing the line-shape theory at these densities requires the creation of a large volume of plasma with very uniform conditions in order to achieve the optical depths necessary to measure the full line profile. These are the first line-shape experiments to utilize purely x-ray heated plasmas and the first to use multi-cm scale samples. Benefits include minimum turbulence and independent control of the plasma density, heating flux, and optical depths. The successful development of this platform will address the WD problem and can be expanded to address molecular effects at low electron temperature, effects of elemental mixtures on line shapes, and effects of correlations in the warm dense matter regime.

Z-Petawatt Driven Ion Beam Radiography Development

151367

Year 2 of 3

Principal Investigator: M. Schollmeier

Project Purpose:

We are performing laser-driven ion beam radiography of an object during a megaJoule-driven discharge of the Z-machine in order to measure the object's electromagnetic field distribution. This will allow unmatched insights into both the target performance for, for example, spherical capsule implosions, magnetic flux compression or astrophysical jet simulations, as well as the machine's performance by mapping the magnetic field distribution with micron spatial resolution. Because of the high magnetic fields and the tremendous amount of x-ray energy created during a discharge, this approach is scientifically and technically very challenging. Required is the capability of creating high ion beam energies (10-100 MeV range) with a short-pulse, high-energy laser system providing intensities well above 10^{20} W/cm². The Z-Petawatt laser (ZPW) has recently demonstrated its readiness for x-ray backlighting, and it can be modified to utilize ion acceleration at the Z-machine by using novel, plasma mirror focusing devices.

New Strategies for Pulsed Power Transmission Lines: from Repetitive to Replaceable to Recyclable

154060

Year 2 of 3

Principal Investigator: M. E. Cuneo

Project Purpose:

Multi-laboratory teams have begun initial experiments aimed at achieving fusion ignition at the National Ignition Facility and demonstrating, for the first time, the scientific feasibility of inertial fusion in the laboratory. Presentations by the Director of the Office of Science and Technology Policy have recently included fusion as an advanced energy option for the first time in many decades. The DOE and NNSA have proposed to start a program in Inertial Fusion Energy (IFE) and have commissioned a multi-year study by the National Academies of Science and Engineering to recommend how this new program should be pursued. New target results and new driver concepts at Sandia have recently led to exciting advances in pulsed power driven inertial confinement fusion for weapons applications.

A nuclear fusion system is the only possible energy source with all the following characteristics: persistence for millennia, nearly carbon free, provides baseload or load-following capability and has potentially twice the on-line availability ($>50\%$) than wind or solar. Availability of nuclear fusion would enhance US energy security.

The most prominent science and technology gap in the application of pulsed-power to IFE systems is the need to have a conducting path for the current between the driver and the target, and to create this path repetitively. We will investigate pulsed power science challenges of rep-rate drivers such as repetitive-transmission line (TL) conditioning and performance, and explore near-term applications such as systems for replaceable-TLs, with longer-term relevance to the most challenging problems of recyclable-TLs for IFE.

There is no inertial fusion energy program presently funded at either DOE or Sandia. This work will lead to attractive point designs for pulsed power IFE fusion power plants that may be able to attract future investments, when such a program is begun in DOE.

Integration of MHD Load Models with Detailed Circuit Representations of Pulsed Power Drivers

155458

Year 2 of 3

Principal Investigator: C. Jennings

Project Purpose:

State of the art magnetohydrodynamic (MHD) models of loads fielded on the Z accelerator are typically driven by reduced, or simplified circuit representations of the generator, while generator models typically couple to simplified representations of the load. The performance of many of the imploding loads is critically dependent on the current and power delivered to them, so they may be strongly influenced by the generator's response to the rising inductance of these loads. Current losses diagnosed in the transmission lines approaching the load are further known to limit the energy delivery, while exhibiting some load dependence. Studying the efficiency with which power may be coupled between the generator and the load in this implicitly linked, rapidly evolving system therefore necessitates the integration of detailed generator and load models. This project is developing an integrated load-generator model to establish a predictive capability that may be used to explore both how existing and next-generation pulsed power drivers may be optimized to support specific loads, and also how loads may be better optimized to the specific response of the generator.

Richtmyer-Meshkov Instabilities in Cylindrical and Planar Geometries on Z **156252**

Year 2 of 3

Principal Investigator: E. Harding

Project Purpose:

The goal of this project is to design an experiment that will produce the Richtmyer-Meshkov (RM) instability in dense plasma by using the large current output of the Z machine. This instability initiates the mixing of plasmas in a wide range of problems that involve large-scale systems such as astrophysical supernovae and smaller-scale systems such as imploding fuel capsules and liners in laboratory fusion experiments. This project's goal is to create a RM unstable experiment where the perturbation growth rate and the degree of mixing caused by the RM instability are diagnosable. One of the important questions is whether modern computer codes and analytical theory can accurately capture the detailed growth and mixing induced by the RM instability. In addition, from a basic science perspective does a dense plasma transition to turbulence in the same way as a cold, non-ionized, fluid? Almost all previous RM experiments in plasma utilized lasers to generate the required shockwave that initiates the instability. Due to the small laser spot size and the relatively small amount of energy delivered to the target, the previous laser experiments did not capture the detailed perturbation growth nor did they achieve a fully turbulent state. We are using two approaches to generate the RM instability on the Z machine. RM could be generated in a planar system that involves the impact of a high-velocity flyer-plate onto a layered target with an embedded perturbation. Or by imploding a cylindrical beryllium shell with interior perturbations, and filled low-density foam, RM could be generated in a cylindrical geometry. Both the planar and cylindrical experiments involve novel target designs and diagnostic techniques that have not been tested previously.

Kinetics of Radiation-Driven Phase Transformations in PZT Ceramics

157693

Year 2 of 3

Principal Investigator: N. W. Moore

Project Purpose:

The purpose of this project is to understand the kinetics of phase transformation of lead zirconate titanate (PZT) ceramics following rapid heating. The only phase kinetics yet measured for PZT are those driven mechanically or electrically along the pressure axis of the phase diagram. Upon heating from room temperature, PZT transforms from a ferroelectric phase (FR1) to a less polarizable one (FR2), and finally to a paraelectric phase (P). A key exploratory aspect is that optical properties that could be used to discern this trajectory are not known for PZT. In particular, structural similarities pose considerable risk in differentiating the rhombohedral FR1 and FR2 phases. This work presents unique opportunities to clarify these differences. The interrogation of these optical properties is, therefore, the thrust of the project. If successful, the kinetic mechanisms could then be explored. Phase dynamics are of broad scientific and engineering importance yet are poorly understood for many materials, including PZT.

Atomistic Modeling of Memristive Switching Mechanisms in Transition Metal Oxides 158699

Year 1 of 2

Principal Investigator: R. J. Bondi

Project Purpose:

In 2008, Hewlett Packard (HP) Labs described a physical implementation of the theoretically proposed, fourth passive circuit element, the memristor. This device exhibits a resistance modulated by the integral of charge transported through it with a hysteretic behavior that permits reversibility. Recent studies on the HP Pt/TiO₂/Pt implementation identified electrochemical reduction of TiO₂ through an applied voltage bias and subsequent migration of charged oxygen vacancies (VO₂⁺) as the likely mechanism driving transformation to less resistive TiO_x phases. Memristive behavior has been generalized across other metal oxide systems with TaO_x exhibiting perhaps the greatest device potential; however, little is known about the mechanism of phase change dynamics during either electroformation or switching for any candidate metal oxide system. For the memristor to evolve into a fundamental integrated circuit (IC) component, an improved understanding of the switching mechanism is beneficial to control both reliability and memory retention, achieve manufacturable device yields and uniformity, increase switching speeds, and understand radiation tolerance margins for Sandia weapons applications.

Recent progress in phase identification suggests that VO₂⁺ migration translates the TiO₂/TiO_x ($x < 2$) phase boundary in order to change device series resistance ($RTiO_2/RTiO_x \sim 10^2$ to 10^3), but questions remain regarding the comprehensive phase space traversed and the essential atomistic/defect dynamics of phase transformation. Thus far, titania-based switching kinetics are not understood since reported switching times (< 10 ns) cannot be explained by expected VO₂⁺ mobilities within conventional drift/diffusion models that are well established for transistors; however, these drift/diffusion models fail to comprehend ionic motion or thermal effects enabling phase change. Since nanometer scale in situ switching observation is impractical via experiment, this work is pursuing an atomistic modeling approach propagating intrinsic defect information from density functional theory (DFT) calculations in candidate metal oxides into an atomistic structure comprising the essential device elements of fabricated memristors for molecular dynamics (MD) simulation.

Laser-Ablated Active Doping Technique for Visible Spectroscopy Measurements on Z

158701

Year 2 of 3

Principal Investigator: M. R. Gomez

Project Purpose:

The intent of this research is to enable high spatial resolution spectroscopic measurements in order to further our understanding of various high energy density plasma experiments. In particular, this project is aimed at allowing better diagnosis of the plasma formation in the post-hole convolute on the Z machine. Plasma formation in the convolute is suspected to cause the significant current losses observed on some Z shots. The evolution of the plasma in the convolute is not yet well understood.

This new capability will allow measurements of extreme environments, like the convolute, which previously have not been accurately probed. Spectroscopic measurements of the convolute may show significant Stark shifting and Zeeman splitting, as well as Stark broadening and possible Doppler shifting.

High spatial resolution spectroscopic measurements can be obtained using carefully designed lens-coupled collection systems and localized tracer elements with favorable emission characteristics. The purpose of this project is to develop both the collection optics and spectroscopic tracer systems such that they can be utilized on the Z machine.

A lens-coupled collection system has been designed and successfully fielded on Z during the last year. This setup allows for submillimeter spatial resolution at the focal plane. Implementation of a spectroscopic tracer will allow for axial spatial resolution on the order of millimeters as well. Presently, the main focus of this project is to develop the localized tracer.

The tracer element is introduced to the system by focusing a high power laser on a thin sample material, which causes the material to ablate and “blow off” into the region of interest. This concept has proven effective in producing an appropriate tracer. However, in order to easily field this system on Z, the laser cannot have an open beam path. This necessitates fiber optic coupling of the laser, which is non-trivial at these laser powers.

Fundamental Studies on Initiation and Evolution of Multi Channel Discharges and their Application to Next-Generation Pulsed Power Machines

158858

Year 1 of 3

Principal Investigator: J. Schwarz

Project Purpose:

Future pulsed power systems may rely on linear transformer driver (LTD) technology. The LTDs will be the building blocks for a driver that can deliver higher current than the Z machine. The LTDs would require tens of thousands of low inductance (<85 nH), high voltage (200 kV DC) switches with high reliability and long lifetime ($>>10^4$ shots). Sandia's Z machine employs 36-megavolt-class switches that are laser triggered by a single channel discharge. This is feasible for tens of switches, but the high inductance and short switch lifetime associated with the single channel discharge are undesirable for future machines.

Thus, the fundamental problem is how to lower inductance and losses while increasing switch lifetime and reliability. These goals can be achieved by increasing the number of current-carrying channels. The rail gap switch is ideal for this purpose.

Although rail gap switches have been extensively studied, each effort has only characterized a particular switch. There is no comprehensive understanding of the underlying physics that would allow predictive capability for arbitrary switch geometry. We propose to study rail gap switches via an extensive suite of advanced diagnostics in synergy with theoretical physics and advanced modeling. Design and topology of multichannel switches as well as discharge dynamics will be investigated. This involves electrically and optically triggered rail gaps and multisite switch concepts.

This research is aimed at gaining a full understanding of the underlying physics that drives the behavior of either optically or electrically triggered rail gap switches. The biggest risk factors are the complexity of the modeling and the fact that some triggering techniques may turn out to be cost prohibitive on a large-scale machine. The research has tremendous payoff because it will provide a comprehensive understanding and predictive capability of high repetition rate, high reliability and long lifetime switches, which is an enabling technology for a realistic pursuit of next-generation pulsed power fusion machines.

A New Capability to Model Defects in InGaAs and InGaP Alloys

158860

Year 1 of 3

Principal Investigator: A. F. Wright

Project Purpose:

Because point defects can adversely affect the performance of semiconductor-based electronic and optoelectronic devices, they have been extensively studied for the past 50 years using a wide variety of experimental techniques. While these studies have yielded a comprehensive understanding of point defects in silicon, significant knowledge gaps remain for point defects in nearly all other semiconductors. Density functional theory (DFT) is capable of filling many of these gaps, and DFT techniques currently exist to obtain information about point defects in both elemental semiconductors and compound semiconductors, including their atomic structures, formation energies, and diffusion pathways and activation energies. However, it is not feasible to directly apply these techniques to semiconductor alloys because defect properties in alloys are position dependent (due to the chemical disorder in an alloy) and explicit calculations would be needed at every possible defect site in the alloy. The purpose of this project is to develop a computationally efficient technique for computing defect properties in alloys and to use this technique to study the diffusion of self-interstitial defects in InGaAs and InGaP alloys. The core of our proposed technique is a “cluster expansion” model that will yield the formation energy of a point defect as a function of the nearby types and arrangement of atoms. We will obtain this cluster expansion by using DFT to compute the formation energies of a defect for a small, representative set of nearby atom types and arrangements, and then fit a set of (cluster-expansion model) parameters to the DFT results. The cluster expansion will then be used to find the formation energy of a defect as a function of position in an alloy, and to obtain the diffusion activation energy as a function of position, from which kinetic Monte Carlo simulations will be performed to obtain the defect temperature-dependent diffusivity.

Investigate Emerging Material Technologies for the Development of Next-Generation Magnetic Core Inductors for LTD Pulsed Power Drivers

158861

Year 1 of 3

Principal Investigator: D. L. Huber

Project Purpose:

The use of magnetic cores in linear transformer drivers (LTDs) creates a significant risk to the success of realizing next-generation pulsed power drivers. Costs are extremely high and fabrication schedules are not aligned to forecasted requirements due to materials utilized and complex manufacturing methods. A breakthrough research and development effort focused on the utilization of emerging advanced high-performance materials for this critical pulsed power component is required to ensure that product performance, cost, and availability meet the requirements of this critical pulsed power driver component.

LTD is the next generation technology for petawatt-output pulsed power machines required for nuclear weapons test and validation, dynamic material properties research, and high energy density physics research and development. For Sandia to remain the lead in this NNSA area we must be prepared with technically sound, well developed, and proven pulsed power machine designs that are cost effective and aligned with DOE/NNSA budgets. Research and development of next-generation capacitors, magnetic cores, and structural components is required to ensure Sandia's position as the lead laboratory in this critical DOE technology.

To accomplish this, the Pulsed Power Sciences Center must identify and develop a high-performance magnetic core for the LTD technology. Sandia must identify or develop a form of Iron (Fe) material that possesses high saturation flux density properties (amorphous, nanocrystalline, or single crystal form) for use in these cores. This is a product area in which the private sector manufacturers of magnetic materials have shown little or no interest due to the unique production requirements (low volume and/or sporadic ordering). Once candidate magnetic materials are identified, we will investigate methods to manufacture them into required shapes for LTD magnetic cores.

Using a Nonlinear Crystal to Optically Measure Pulsed Electric Fields in Radiation Environments

159299

Year 1 of 2

Principal Investigator: T. M. Flanagan

Project Purpose:

This project will pursue the creation of a completely optical electric field sensor to be used in a pulsed radiation environment. The advantage of an optical sensor is that it only minimally perturbs the electric field that is to be measured. There are no electronics associated with the measurement. Thus, it is less vulnerable to electrical noise associated with pulsed x-ray facilities.

The sensor is intended for experiments where cavities are exposed to x-rays, such as those produced by the Z facility or similar accelerators. While optical E-field sensors have been used before, their operation in a pulsed radiation environment poses new risks and challenges that have not been addressed. These x-ray sources produce a large energy fluence and are short lived ($\ll 1$ microsecond), as are the electric fields they induce. Thus, the field sensor must be durable and have a fast response (nanoseconds).

The sensor will exploit properties of nonlinear crystals that are commonly used as optical switches or harmonic generators of laser light. When a large E-field is applied to these crystals (a few kV/cm or less), they can modulate laser light at tens of GHz or less. In the proposed application, x-rays interacting with the cavity produce the E-field. The modulation of light passing through the crystal would indicate the E-field strength.

Successful development of this sensor would result in a new method of measuring cavity electric fields in the Z accelerator and other x-ray sources. Previous electrical E-field sensors did not consistently provide reliable results. Exposed electrodes were too sensitive to charge collection from the high-energy electrons, thus compromising the measurement. Our proposed optical E-field sensor could allow for direct E-field measurements that were not previously available.

Analysis of Defect Clustering in Semiconductors using Kinetic Monte Carlo Methods 159305

Year 1 of 2

Principal Investigator: B. D. Hehr

Project Purpose:

The transient degradation of semiconductor device performance under irradiation has long been an issue of concern. Neutron irradiation can instigate the formation of quasi-stable defect structures, thereby introducing new energy levels into the bandgap that alter carrier lifetimes and give rise to such phenomena as gain degradation in transistors. Typically, the initial defect formation phase is followed by a recovery phase in which defect-defect or defect-dopant interactions modify the characteristics of the damaged structure. These interactions are facilitated both by thermal diffusion and by capture or emission of charge carriers — a mechanism specific to semiconductors.

Atomistic simulation techniques such as molecular dynamics (MD) have been used successfully to generate initial defect maps in semiconductors; however, such techniques lack characterization of electronic charge states and operate on a timescale far too short for studies of defect evolution. The purpose of this project is to develop a kinetic Monte Carlo (KMC) code capable of modeling both thermal and carrier injection annealing of group IV or group III-V initial defect structures. Treatment of the injection annealing is foreseen to necessitate a model of the semiconductor device physics along with a coupling of the device model to the external radiation environment (e.g., to account for induced photocurrents).

Standard computational annealing techniques encompass neither injection annealing nor the time-dependent interplay between an impinging radiation environment and the microscopic annealing process. The challenge of investigating these phenomena in a coupled manner yields commensurate dividends in the fidelity and specificity of the resulting defect distributions with regard to the spatial particularities of a semiconductor device. Consequently, the proposed project has the potential to enhance standard KMC annealing algorithms with new capabilities.

Time-Dependent Resistivity of Millimeter-Gap Magnetically Insulated Transmission Lines Operated at Megampere/Centimeter Current Densities

164759

Year 1 of 3

Principal Investigator: B. T. Hutsel

Project Purpose:

Magnetically insulated transmission lines (MITLs) are commonly used in the final stages of pulsed power systems to transfer power at high voltage and current to the physics package load. Future pulsed power systems, which will deliver greater power to the load, will require MITLs to transfer power at greater voltage and current. Minimizing current loss within the MITL will be a critical design issue for these larger pulsed power systems.

This project will investigate current loss in a MITL at megampere/centimeter lineal current densities due to gap closure. Gap closure occurs when plasma forms within the MITL anode-cathode gap providing a conductive path for current to be shunted away from the load, resulting in reduced power transferred to the load.

Current loss within a MITL will be characterized as a function of gap distance, peak current, peak voltage, and pressure in the MITL gap. Surface chemistry will be considered and gap closure will be investigated relative to vacuum surface conditions and MITL-electrode cleaning procedures. In addition to experimental results, a theoretical model of gap closure will be developed with the aid of particle-in-cell (PIC) simulations.

The proposed research will extend existing knowledge of MITL behavior at high lineal current densities. The main technical challenges include quantitatively characterizing the vacuum surface conditions to determine their effect on MITL current loss. Development of a theoretical model of gap closure through combination of experimental results and PIC simulations will aid in the design of MITLs used in future pulsed power machines.

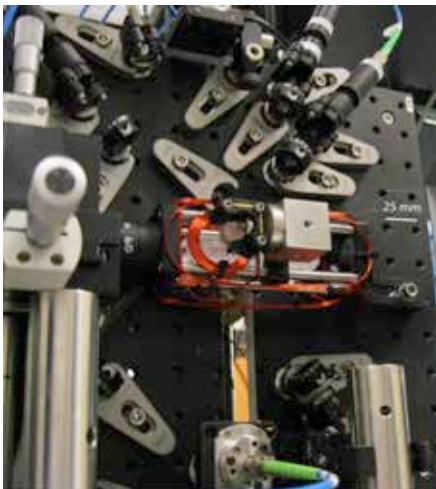
A systematic study focused on gap closure, combined with new simulation capabilities, has yet to be performed. The experiments will yield a more thorough understanding of gap closure within a MITL. Results from characterizing MITL performance at high current densities will aid in designs of future pulsed power accelerators that will be necessary to extend high energy density physics (HEDP) research.

DEFENSE SYSTEMS AND ASSESSMENTS INVESTMENT AREA

This investment area funds both fundamental and applied research into science and technology that is or can be rendered applicable to national defense — from software to assist the human intelligence analyst by filtering and more-coherently organizing intelligence streams, to virtual training scenarios for analysts and warfighters to a variety of improved detection-science and -technology solutions for chemical and biological threats to populations, and even to improved robotic agents to mitigate risks to soldiers and civilians in dangerous scenarios. Through these and other initiatives, projects in this investment area contribute to national defense and homeland security — and, therefore, help diminish the global threat of terrorism.

Matterwave Interferometer for Seismic Sensing and Inertial Navigation **Project 151275**

In recent years, the performance of inertial navigation systems has reached a plateau due to the limits of available sensor technology. Light-pulse matterwave interferometry is widely recognized to be the next advance for inertial measurements. This project is pursuing a tabletop demonstration of the first high-bandwidth (100 Hz) matterwave gyroscope/accelerometer, which promises to be a more-rugged device by comparison to existing technology.



For inertial navigation, this technology has the potential to provide a measurement unit exceeding the capabilities of current navigation grade sensors while occupying the same form factor. For seismometry, there is potential for improvement in earthquake/explosion discrimination, as well as characterization of underground facilities.

Prototype of the instrument

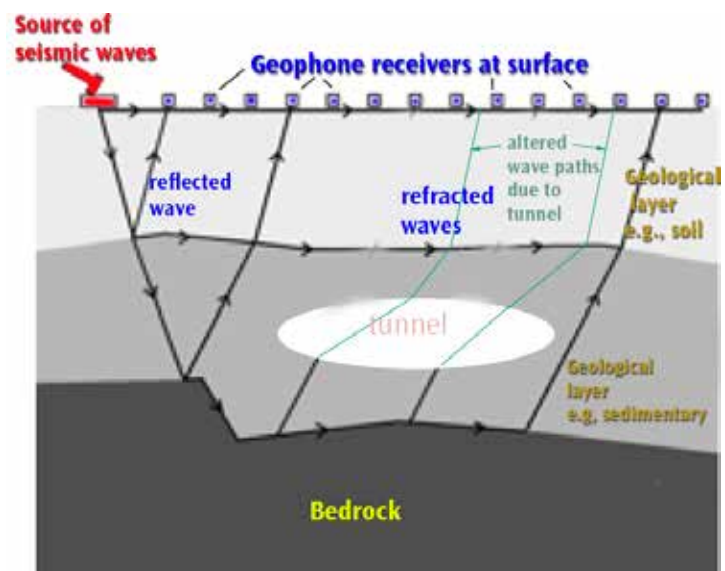
Improving Shallow Tunnel Detection from Surface Seismic Methods Project 156137

Detecting underground structures from above ground—such as tunnels and buried ordnance (e.g., mines)—is a difficult endeavor. This project is pursuing the modification of seismological methods for solving this detection problem.

The principles underpinning seismology methods are similar to those in optics, where Snell's Law tells us that because the speed of light rays is different in different media, light rays bend or refract when passing from one medium to another. This bending also occurs for acoustic waves traveling from air into the soil and from the soil into deeper layers of the earth, such as sedimentary rock and bedrock. By generating acoustic waves at the surface and monitoring—via an array of “geophone” detectors—the collective energy (seismic) waves reflected by the underground geology, geophysicists can map out the underground layers at which waves are either reflected or refracted. If a tunnel is located within those layers, the pattern of wave reflection and refraction should change as waves travel from geological layers and into the airspace of the tunnel or vice-versa. When processed by software algorithms, such changes in wave patterns should be able to reveal a tunnel's existence and location.

The problem with these methods is that they frequently don't work precisely, and this project is focusing-in on the reasons for this disparity. It has pinpointed a quite important factor, namely hydrology, that is the degree of water saturation of different layers—from soil to the pores in rocks. Building the tunnel creates fractures in the surrounding rock, thereby “dulling” what might otherwise be a sharp transition with respect to seismic wave refraction. Even more important, these fractures create more pores that can change the degree of water saturation.

The computer codes used by the oil and gas industry for their subsurface operations are not much help because of the greater depths at which they are investigating; at those depths, pressure is much greater, rocks are more consolidated (less porous), and changes in hydration are less of a factor. Hence, a large aspect of this work has, focused on hydrology codes. Because it has a much better handle on the appropriate applicable hydrology codes, the project is now able to translate that understanding into improved seismology codes that take the hydrology into account.



Schematic drawing to illustrate the general concept that the presence of an underground tunnel would be expected to change the wave paths of some of the returning seismic waves.

Defense Systems and Assessments Investment Area

2D Tracking of Maneuvering and Closely Spaced Targets and Fusion into 3D Tracks 141541

Year 3 of 3

Principal Investigator: T. J. Ma

Project Purpose:

In time-critical tracking problems, one or more moving objects may be observed by multiple sensors. The sensor data are processed in real-time, with the goals of discriminating the separate target objects, tracking their progress in each sensor's dynamic field of view, and combining information across sensors to 3D object positions as a function of time. Maneuvering targets presents a great challenge to both 2D and 3D tracking. When a target performs a maneuver, its dynamic motion can be very different from previously estimated motion. If the maneuver behavior is not well modeled, it will cause a large error in the target's estimated position, velocity, and acceleration, and potentially a single Kalman filter will not track the target at all. Using multiple filter models to estimate the target's overall dynamics is appealing but deciding when to switch between models imposes a challenge. Fusion of multiple sensor, 2D detections, and tracks into 3D position estimates is an additional challenge. Individual sensors can have different biases and random errors, and may produce different sets of real, false, or missing tracks. These errors and misassociations create a significant challenge when determining the true targets that all the sensors are observing. Over the past two years, this project has made significant technical advancements in developing both 2D and 3D trackers with Interacting Multiple Model (IMM) algorithms and closely spaced objects (CSO) tracking. Up to this point, the flow of data has been strictly from the 2D tracker to the 3D tracker. In the final year of this project, one of our key focuses is investigating the effectiveness of providing feedback from 3D tracking to 2D tracking. Additionally, our tracking simulated software named SANTRAC will be enhanced so that complex simulated scenarios can be generated and thorough tracking performance evaluation can be conducted.

Summary of Accomplishments:

In the area of 2D tracking, we have successfully developed a multiple-hypothesis tracking (MHT) algorithm and implemented our solution to the CSO problem. Unlike traditional MHT algorithms where the process of hypothesis formation is NP-hard, our score-based prioritization hypothesis formation approach significantly reduces computational overhead, allowing the algorithm to converge into a good enough solution in a least amount of time, thus making our algorithm suitable for near-real-time processing. We have demonstrated significant improvements in CSO tracking when compared with single-hypothesis tracking. We have observed a tracking improvement of 25% in a diverse collection of datasets. In the areas of maneuvering-object tracking, we have successfully developed various target models and implemented the IMM filtering technique. The IMM tracker is capable of detecting maneuvering targets and has demonstrated up to 40% reduction in position error during the course of maneuver. In the areas of 3D tracking, a tracklets-based fusion approach was developed to fuse 2D tracks from individual sensors into 3D tracks. Simulation software, named SANTRAC, has been developed for tracking simulation and performance evaluation. Finally, a feedback loop has been implemented from the 3D tracker to the 2D tracker. In our simulation, we have demonstrated that, when a target is not observable by an individual 2D sensor but observable by other 2D sensors, state estimates generated by fusion of other 2D sensors can be feedback to the 2D tracker to help improve track performance.

Significance:

Remote sensing plays an important role in national security missions of DOE and various other federal agencies that sponsor Sandia work. This research benefits existing and future programs designed to provide time-critical intelligence information to a diverse user community. This project will also advance scientific knowledge by the novel combination of several advanced technologies in the general field of tracking with remote sensors.

Hybrid Femtosecond/Nanosecond Pulsed Laser Machining 141595

Year 3 of 3

Principal Investigator: B. H. Jared

Project Purpose:

There is an existing demand at Sandia for versatile micromachining techniques that precisely and rapidly section composites of different known and unknown stoichiometry. Such materials, which may include metals, dielectrics, semiconductors, and organics in the same volume, are not adequately addressed with conventional methods due to a distinct lack of material selectivity or other limitations. While laser-based micromachining methods involving a single-pulse duration have been pursued as a viable alternative to mechanical and chemical sectioning, no single laser source provides the combination of rapid processing, material selectivity, and material versatility required for successful processing of all composites. To address these issues, we have researched and developed a hybrid pulsed-laser technique with in-situ chemical characterization for high-throughput, feedback-controlled processing.

Summary of Accomplishments:

Work across project milestones was achieved during the final year. The integration of optical and electrical hardware enabled spatial and temporal control of femtosecond (fs) and nanosecond (ns) laser pulses and of laser-induced breakdown spectroscopy (LIBS) analyses. Closed-loop control of all system hardware components was integrated and implemented in LabView. Machining rates and material damage were examined under relative temporal spacing of the fs and ns laser pulses.

Significance:

Sandia is a leader in developing advanced materials engineering and analysis techniques that provide leading-edge capabilities in microelectronics, microelectromechanical systems (MEMS), photovoltaics, etc., for DOE, NNSA, and other national security customers. The development of hybrid laser sectioning methods that address a large variety of materials, including composites, will enhance our ability to address future needs of these customers as well as advance the mission of scientific discovery and innovation.

Remote Sensing of Gases for Greenhouse Gas Monitoring and Treaty Verification 141606

Year 3 of 3

Principal Investigator: J. A. Mercier

Project Purpose:

The purpose of the project is to investigate gas filter correlation (GFC) radiometry as a technique for optical remote sensing of a suite of gases that are of special interest for Sandia's Remote Sensing and Verification Program (RSVP). The primary gases are carbon dioxide (CO₂), carbon monoxide (CO), and methane (CH₄). All of these gases have absorption features in the shortwave infrared spectral region. The major objectives are to model all aspects that would affect performance of airborne and space based GFC imaging radiometers and to design a theoretical optical sensor that measures relevant levels of effluents to verify compliance with treaties that could eventually regulate greenhouse gas emissions.

This work presents several unique challenges. CO and other effluents have spectra that consist of very narrow, widely spaced lines. Very high spectral resolution is required to isolate absorption by these lines. CO₂ and CH₄ are relatively uniformly distributed around the globe, and, therefore, concentrations of these gases must be measured with very high precision in order to draw useful conclusions about local sources. GFC radiometry combines high spectral resolution with high throughput and high signal-to-noise ratio to meet all of these demands. However, scene clutter and interference from water vapor remain as significant issues for this approach. While GFC radiometry has a rich heritage of remote sensing of atmospheric trace gases in the stratosphere and mid-troposphere, the difficulties of working in the SWIR solar reflective range and measuring gases in the lower troposphere have not previously been overcome. By tackling these issues, this project will enable the RSVP program at Sandia to meet mission needs for the DOE and other government organizations.

Summary of Accomplishments:

A pair of radiometric models of the GFC remote sensing process was developed under this project. The primary difference between the two models lies in how the amount of the gas of interest in the scene is perturbed. One model assumes that the gas of interest is distributed throughout the atmospheric column according to some prescribed profile of concentration as a function of altitude, which is a good approach for predicting the performance of a sensor that would make global measurements of the column amount of greenhouse gases. The other model perturbs the concentration profile by adding a plume with a specified concentration, which is a good approach for predicting the performance of a sensor that would inspect natural-gas pipelines for leaks.

A detailed modeling capability for the simulation of chemical plume effluent transport has been created. The motivation is to apply advances in computational fluid dynamics, visualization, and data processing for the analysis of plume dispersal. The goal is to better understand aerosol dispersal behavior as it relates to remote sensing and data interpretation. Several Fuego aerosol dispersion models that released various gases have been developed. Fuego is a mature, massively parallel computational fluid dynamics code that addresses plume transport and mixing at a far finer scale and with far more detail than any existing Gaussian or puff-based transport models.

Preliminary design work was carried out for a notional airborne sensor. A basic optical layout was created using the Zemax ray trace program. A basic mechanical layout for mounting the sensor in an airborne pod on a MQ-9 Reaper unmanned aerial vehicle (UAV) was created. The pod is an aerodynamic container that attaches to an aircraft's mounting pylons. The optical and mechanical

designs were all completed to fit within the UAV pod envelope and performance predictions for the notional design have been completed.

Significance:

The purpose of the project was to investigate gas filter correlation radiometry as a technique for optical remote sensing of a suite of gases that are of special interest for Sandia's Remote Sensing and Verification Program. The primary goals of this work were to build a model for radiometric calculations and to use that model to predict sensor performance for conceptual airborne and space-based gas filter correlation radiometers. All of the major goals of this R&D effort have been accomplished, and there now exists a unique capability to model effluents and predict GFC sensor design concept performance against those effluents. This research aligns with the climate change mission of DOE.

Use of Phase Conjugation in High Energy Laser Systems 141613

Year 3 of 3

Principal Investigator: D. E. Bliss

Project Purpose:

Systems based on propagating high-energy laser light through aberrating media would benefit from technologies that mitigate the aberrating effects. Higher energy can be achieved by building a bigger laser or by combining beamlets from multiple smaller lasers. However, both techniques suffer from increased optical aberrations associated with larger-aperture gain media and multi-aperture combination. The ability to correct aberrations would allow the available laser energy to be focused with more intensity. Simple methods to combine beams using passive optics (mirrors, splitters) do not ensure mutual coherence, resulting in a beam with a non-ideal wavefront and poor Strehl ratio. To address this need, we are investigating the limits of phase-conjugated (PC) approaches that rely on Stimulated Brillouin Scattering (SBS).

Summary of Accomplishments:

The high pressure SBS cell has been a stable and robust tool in the laboratory and for field tests. In the last year of the project, we conducted field tests at an outdoor laser range (100m). The laser, stimulated Brillouin scattering (SBS) receiver, and diagnostics were moved from the laboratory to the outdoor range. The architecture of the experiment was changed to broadly illuminate an object and amplify the return from a glint, phase conjugate the amplified light, and resend it back to the target to illuminate only the glint. With natural convection and turbulence from the boundary layer over the asphalt, the SBS process worked flawlessly with a structure coefficient for the index of refraction, $C_n^2 \sim 2 \times 10^{-14} \text{ m}^{-2/3}$. In order to discover the C_n^2 limit that the SBS could correct, large commercial outdoor space heaters (600,000 BTU/h) were added to the path to increase turbulence. We could adjust the positioning of the space heaters to achieve C_n^2 from 10×10^{-14} to $10 \times 10^{-10} \text{ m}^{-2/3}$. SBS could successfully correct for atmospheric aberrations at the range at a level of $C_n^2 \sim 1 \times 10^{-12} \text{ m}^{-2/3}$ as measured by a commercial scintillometer although not without significant amplitude jitter in the amplified resent beam. Far-field cameras indicated a corresponding D/r_0 of ~ 20 for the 100-mm illumination beam. The smallest glints that the amplified SBS process could lock onto were $\sim 5 \text{ mm}$ in diameter.

Significance:

Understanding the capabilities and limits of SBS methods for phase conjugating and combining high-energy laser beams will enable Sandia to assess the potential capability and create applications for our own scientific programs. Our results indicate that SBS PC is an effective means to correct aberrations due to aberrated media.

Quantum-Enhanced Technologies (QET) 141930

Year 3 of 3

Principal Investigator: G. Biedermann

Project Purpose:

Quantum effects have a wide variety of applications in computation, communication, and metrology. To explore practical quantum enhanced technologies, we are investigating quantum metrology in neutral atom systems, such as inertial sensors and microwave clocks. The typical lower noise boundary on measurements of a two-level quantum system is given by standard quantum limit (SQL). This limits the signal-to-noise ratio (SNR) to $\text{SNR} = \sqrt{N}$, where N is the number of atoms. However, using the technique of spin squeezing, it has been demonstrated that one may increase uncertainty in one spin quadrature in exchange for decreasing uncertainty in another metrologically relevant quadrature to result in $\text{SNR} = N$, which is known as the Heisenberg limit. This can deliver remarkable gains for typical systems that use $N = 10^4$ to 10^7 atoms. However, to realize the gains of quantum-enhanced metrology, one must first realize high fidelity measurements of quantum systems. This fidelity is often limited by sources of technical noise in the system, which must be characterized and mitigated. The thrust of this project is to experimentally and theoretically understand these limits in order to design practical systems that move beyond the SQL. This work is done in collaboration with the University of New Mexico.

Summary of Accomplishments:

The first major task of this project has been achieved, that being the development of a functioning experimental apparatus for microwave spectroscopy of cold-atom hyperfine levels. We developed specific control and measurement software and field programmable gate array (FPGA) control for microwave pulse generation in order to complete our studies on an existing cold-atom trapping system. The apparatus allows for the laser cooling, coherent manipulation, and electronic state detection of approximately 100,000 neutral rubidium atoms. In achieving our second milestone, we have studied microwave-induced Rabi flopping, the basis for microwave clocks. By suppressing technical sources of noise, we have achieved, for interrogation times of up to 3 ms, a SNR close to the maximal possible quantum mechanical value (SQL). We have also theoretically modeled and experimentally measured inefficiency mechanisms in stimulated Raman spectroscopy, the basis for atom-interferometer inertial measurements. We have found that these loss mechanisms limit the SNR to well below the SQL. We have used this study to theoretically evaluate the efficacy of multiple pulse sequences for enhancing sensitivity. Finally, we performed a paper study of approaches to surpassing the SQL in these systems.

Significance:

Enhancements from quantum metrology may be applied to two-level systems, which are known for their exceptional performance in inertial sensing, clocks, metrology and spectroscopy. As a specific example, accurate inertial measurements are essential in a region where global positioning system (GPS) may be denied. Furthermore, these may be used for surveillance and reconnaissance, characterization of underground facilities, characterization for defeat, navigation of unmanned platforms, prompt global strike, and precision conventional munitions delivery, all key missions important to DoD. Precision navigation also relies on high-performance time keeping in compact packages. The ultimate performance of such technology requires understanding sources of noise and mitigating them to reach the Heisenberg limit.

A Model-Based Approach for Detection and Avoidance of Subversion in System Development Tool Chains

151170

Year 3 of 3

Principal Investigator: B. K. Eames

Project Purpose:

The Defense Sciences Board (DSB) has studied the national security impact of the globalization of the information technology (IT) industry and, in particular, the loss of US control of the supply chain of both integrated circuits and software for critical applications. The DSB concluded that several grave threats exist to the development of secure systems when components, development tools, and/or manufacturing facilities are not created and maintained by trusted sources. However, “trusted” design processes can be prohibitively expensive and may yield inferior performance.

The development of modern systems requires sequences of development and analysis tools in order to produce correctly functioning systems. From a security perspective, toolflows offer adversaries multiple points of entry through which minor alterations can be deployed, with the goal of subverting the system while it executes. The question is raised as to whether a trusted system can be developed using a toolflow where one or more of the constituent tools are not developed and maintained by a trusted source.

Security researchers have begun to explore both the technical and security risks of component technologies developed from an uncontrolled supply chain. However, the risks of untrusted development tools and their potential to introduce paths to system subversion have been largely ignored.

The primary goal of this project has been to develop techniques to determine whether malicious alterations have been made to a design during synthesis.

Summary of Accomplishments:

In FY 2012, we continued the work of evaluating commercial tools as a means of detecting the presence of malicious design alterations inserted at synthesis time.

We continued the analysis of a hardware Trojan to not only detect that a hardware Trojan was present but to determine the location of the Trojan.

We expanded the scope of evaluation to include several hardware Trojan circuits obtained via the NYU-Poly Cybersecurity Awareness Week (CSAW) Embedded Systems Competition from 2009, where students composed Trojan attacks. The resulting circuits were made available publicly.

Significance:

Several federal agencies have identified the risks associated with supply chain management for secure systems. Particularly, DHS, the White House, DoD, and Defense Advanced Research Projects Agency (DARPA) have identified relevant risks. This research has called attention to an area in the trusted integrated circuit supply chain that is currently uncontrolled and has proposed an approach to help mitigate risks associated with using uncontrolled commercial design tools to support trusted circuits. If applied in the proper context, the results of this research will bolster confidence in high assurance, trusted systems development, including DOE’s mission for nuclear stockpile maintenance.

First Principles Prediction of Radio-Frequency Directed Energy Effects 151263

Year 2 of 3

Principal Investigator: L. D. Bacon

Project Purpose:

Radio-frequency directed energy (RFDE) is demonstrating potential for application in many DoD and DOE mission areas. Systems are being developed for use by at least three services and the DOE. Its acceptance, however, is hampered by the lack of first-principles understanding of RFDE effects on electronics. At present, RFDE mission planning is semi-empirical. The uncertainty in the details of the electronic systems in modern targets of interest (improvised explosive device triggers, for example) and the very rapid rate of change in the consumer electronics used in these systems make the results from this semi-empirical approach highly perishable at best or, at worst, irrelevant by the time it is available. Empirical models give us an understanding of what happens with a specific scenario. Naturally, they are limited in how far they can be interpolated or extrapolated beyond the data upon which they are based. What is needed is the ability to predict RFDE effects from first principles, validated against measurements of example systems. First-principles models give us an understanding of why a scenario leads to the results it does. They can be interpolated or extrapolated as far as the physics they are based on remains valid. This ability will allow the details of the target that dominate the response to be identified — something that cannot be done using measurements alone — and their impact on the variability of the response and on effect margins to be addressed. This project will provide that capability as far as it is practicable today.

To our knowledge, no one has yet put together a first-principles estimate of the full RFDE effects process. Some in the community do not believe that it is possible. Our experience indicates that it is likely to be possible and that the insights gained will be well worth the effort even if it is not.

Polarimetric Change Detection Exploitation of Synthetic Aperture Radar Data 151264

Year 2 of 3

Principal Investigator: R. Riley

Project Purpose:

Synthetic aperture radars (SARs) perform intelligence, surveillance, and reconnaissance (ISR) missions by directly observing signatures of features in a scene containing activities of interest and/or by indirectly observing the evidence of activities of interest via change signatures that are present in multi-collect coherent change detection (CCD) products. The ability to detect activities via the change signatures alone is of great benefit to many applications and is utilized extensively on existing fielded airborne SAR systems. However, it can be difficult, even intractable, to classify the underlying cause of the change signatures, especially in high-change clutter scenes. Disparate changes from various mechanisms frequently form one contiguous change signature, especially if several hours pass between collections, making it impossible to detect or discriminate for the change signatures of interest.

SAR systems that exploit polarimetry are already fielded to decompose a scene into terrain types, vegetation cover, and presence of man-made objects; however, we are not aware of any application of this decomposition to CCD classification. Given Sandia's current real-world experience with CCD and associated limitations when utilizing single-polarization airborne SARs, it is a natural next step to consider using fully polarimetric classification to classify CCD change signatures.

This research will investigate the utility of polarimetric-based classification of scene content, as well as changes in underlying polarimetric signatures, to enable change signature discrimination and classification.

Ultra-Thin, Temperature-Stable, Low-Power Frequency References 151266

Year 2 of 3

Principal Investigator: R. H. Olsson

Project Purpose:

We are developing a thin ($<100\mu\text{m}$), temperature-stable (<20 parts-per-billion [ppb]), low-power ($<10\text{mW}$) frequency reference with crosscutting applicability across Sandia's missions. Traditional low-noise oscillators are based on vibrations in quartz crystals. While a mature technology, the large size and mounting of quartz crystals presents important mission barriers including: reducing oscillator thickness below $400\mu\text{m}$, ovenizing for maximum temperature stability at low power, and shock-induced frequency shifts arising from the large crystal mass. While commercial microelectromechanical systems (MEMS) oscillators are thin and shock tolerant, they utilize weak electrostatic transduction resulting in poor phase-noise performance not suitable for communications systems. Recently, Sandia has demonstrated aluminum nitride (AlN) MEMS oscillators with 40dB lower phase noise than commercial MEMS oscillators. While initial results are promising, the temperature sensitivity, 2 parts-per-million (ppm)/C, is too high for precision oscillators. The small volume (microresonators are $2\mu\text{m}$ thick compared to 100's of microns for quartz) and substrate isolation (microresonators are suspended above the substrate by narrow beams for acoustic/thermal isolation) provides a new platform for ovenizing oscillators at revolutionary low power levels ($<2\text{mW}$ compared to 1.5W for quartz). Ovenized oscillators are the gold standard for frequency stability where heaters and temperature sensors are used to maintain the oscillator at a constant temperature above ambient. In this work, we are integrating thin film heaters and temperature sensors directly on AlN microresonators to form ovenized oscillators operating from 10-1500 MHz. We are investigating through modeling and experimentation ovenized resonators with different anchoring suspensions, heaters, and sensors to minimize oven and circuit power while maintaining resonator performance and maximizing temperature stability. We are implementing low-power oscillator and oven control electronics, first at the circuit board and later at the integrated-circuit level. This project will demonstrate a multi-frequency low-noise oscillator technology with unprecedented frequency stability over temperature ($<20\text{ppb}$) at this size and power.

Efficient Thermal-Neutron Detection using Gadolinium Conversion Layers 151267

Year 2 of 2

Principal Investigator: M. Allen

Project Purpose:

Some types of special nuclear material (SNM) emit both gamma and neutron radiation. Neutron detection is considered a more robust means of determining the presence of SNM for two main reasons: 1) neutrons are more penetrating than the low-energy gamma rays specific to most SNM and 2) there are fewer natural and man-made sources of neutron radiation, which makes the detection of neutrons more significant.

Helium-three (He-3) gas-filled tubes are ubiquitous for thermal-neutron detection. High efficiency and low sensitivity to gamma radiation have made He-3 tubes the neutron detector of choice for decades. However, He-3 is increasingly scarce and expensive to acquire due to a recent increase in demand and its very limited production. Therefore, new efficient neutron detection technologies are urgently needed.

We propose to develop a thermal-neutron detector based on materials that have high probability of absorbing neutrons and then emitting energetic electrons. Gadolinium (Gd) has a very high neutron-absorption cross-section, and emits energetic “conversion” electrons following neutron absorption. The emitted electrons have energies ranging from tens to hundreds of kilo-electron volts (keV) and are emitted (at various energies) up to 60% of the time following neutron capture. The measured electron signal produced from such a detector will be directly proportional to the incident neutron flux.

Due to the high neutron-absorption cross-section and internal conversion coefficient of Gd, 30 - 40% intrinsic efficiencies are possible. Furthermore, this solid-state detector should be scalable to large areas to achieve a high absolute efficiency.

The development of a successful prototype will require creative integration of several identified phenomena. Conversion electrons have moderate energy and are difficult to measure. The ability to discriminate thermal neutrons from other radiation sources will require integrating various technologies to collect, focus, amplify, and analyze conversion electrons.

Summary of Accomplishments:

The goal was to couple natural gadolinium with commercially available micro-channel plates (MCPs) in order to construct a large-area thermal-neutron detector. It has been known for decades that several isotopes of gadolinium (specifically gadolinium-155 and gadolinium-157) have the highest naturally occurring cross-section for thermal-neutron capture. After capturing a neutron, these isotopes give off radiation in the form of x-rays, gamma rays, and electrons. Coupling gadolinium to MCPs capable of detecting these radiations could produce a viable neutron detector. Constructing an array of such detectors would make the system scalable to large areas.

Throughout the course of this project, we were able to measure the conversion electron spectrum from five different thicknesses of natural gadolinium foils. By summing the number of counts between 0 and 250 keV, an electron conversion count rate was determined for each foil thickness. By examining this data, we determined an optimum foil thickness. This thickness is most appropriate for maximum absorption of thermal neutrons while remaining sufficiently thin for the generated conversion electrons to escape the foil and be detected by the charge particle detector.

Our experimental results were modeled using the Monte Carlo code GEANT4. There is some discrepancy between the results we achieved using different versions of GEANT4. Using GEANT4.9.3.p01, we were able to model the experiment and achieve reasonably good results with respect to the production of conversion electrons. However, we were not able to accurately model the production of x-rays associated with the conversion electron production process. In an attempt to model all of the necessary physics, we upgraded to the latest version of GEANT, GEANT4.9.5.p01. Using this version of GEANT, we were able to accurately model the production of x-rays, but not the production of gamma rays and conversion electrons associated with neutron capture in gadolinium.

Significance:

The development of a thin-film process for gadolinium will enable gadolinium-foil based detectors. Measurements of conversion electrons from these films inform design of neutron detectors in the future. The nation is still in need of novel neutron detectors that do not require helium-3. This project was a good step forward on the road to development of large-area or small-scale neutron detectors that do not require helium-3, a priority for NNSA and also important for DOE's mission for discovery of fossil fuels sources.

Trusted Execution Methodology · Payload / Operating System (TEM·P/OS) 151270

Year 2 of 3

Principal Investigator: K. Robbins

Project Purpose:

Cyber warfare targeting military systems from adversaries and nation states is an increasing concern. Examples of this include cyberespionage, data intrusion/interception, subversion, malware, denial-of-service, hardware/software Trojan horses, spoofing, jamming, and network attacks. Currently most cybersecurity initiatives primarily focus on non-space systems such as those for weapons and terrestrial systems.

Developing a trusted software architecture for space-based systems is complicated by unique characteristics of the flight segment, including a legacy flight software heritage largely ignorant of security concerns; the inability to access or recover flight hardware once placed in service; size, weight, and power constraints; and the inherent nature of remote command/control and large data collection.

We will address the challenges of developing a trusted software architecture for space-based systems by co-designing a new payload operating system for flight applications and a fully integrated security architecture that leverages Sandia's cybersecurity expertise to meet the specific security concerns of these systems.

The payload operating system will provide the capabilities needed to manage flight software applications on next generation node-based reconfigurable processing architectures, including the facilities to manage the flight hardware, deploy and configure applications, monitor the system and applications for anomalous behavior, and detect/recover from failures. We will research, develop, and demonstrate automated deployment/configuration algorithms to "place-and-route" or assign software components, the basic building blocks of applications, to available processing nodes subject to power, performance, and reliability constraints.

Given the central role this payload operating system will have in future space-based systems, it is critical that the security architecture be an integral part of its development. We propose to research and develop a security architecture primarily focused on protecting the flight payload architecture. Efforts will focus on methods to enhance cybersecurity of data processing modules, pointing and control, and data downlink from design to deployment. We will look at including trust anchors in the payload that will detect and prevent such attacks.

Matterwave Interferometer for Seismic Sensing and Inertial Navigation 151275

Year 2 of 3

Principal Investigator: G. Biedermann

Project Purpose:

In recent years, the performance of inertial navigation systems has reached a plateau due to the limits of available sensor technology. Light-pulse matterwave interferometry is widely recognized to be the next advance for inertial measurements. Demonstrations measure both rotations and accelerations with outstanding fidelity, stability, and intrinsic accuracy. In seismic sensing, a six-axis matterwave sensor can potentially discriminate between and characterize natural and manmade sources (such as underground facilities and explosions) in new ways as well as independently infer wave speed and direction to reduce event location uncertainty. Current atom interferometers are large, delicate, bandwidth-limited to a few Hz, and untenable for rugged seismic and navigation applications. We are pursuing a tabletop demonstration of the first high-bandwidth (100 Hz) matterwave gyroscope/accelerometer, which may enable a broadband and reasonably rugged device. We will evaluate this technology with input from in-house experts in both the navigation and seismology user communities to lay groundwork for a full system development program. We will operate the interferometer in a new short time-of-flight regime enabling a small 10-cc physics package. We anticipate two orders of magnitude gain in data rate and new opportunities for reductions in size and system requirements. A new property of this approach, heretofore unseen with matterwave sensors, is that the orientation can, in principle, be rotated with respect to gravity without severely affecting the performance. Using two counter-propagating, short time-of-flight interferometers, we can simultaneously measure accelerations and rotations at a high data rate. During a short ~ 10 -ms free flight, a light-pulse atom-interferometer sequence determines the platform rotation rate and acceleration with respect to the pristine atom proof mass. We forecast that this concept can achieve sensitivities of 10 nano-g/rtHz for accelerations and 12 nano-rad/s/rtHz (42 micro-deg/rthr) for rotations, far exceeding navigation grade metrics.

Spectro-Temporal Data Application and Exploitation

151276

Year 2 of 3

Principal Investigator: J. K. Roskovensky

Project Purpose:

Prism and grating components that disperse light to produce high-spectral-resolution data could be used to distinguish objects based on spectral characteristics. These dispersive components are contained in Sandia-built sensors without attached mission requirements due to their uncertain utilization. In this project, we propose to determine the potential capability of these new sensors by characterizing the range of apparent signatures of targets of interest to civilian, government and military commanders, and to assess their respective mission performance. This will be achieved through the unique position that Sandia has with respect to sensor design, testing, and data availability and through the Sandia special technical capabilities in phenomenology, modeling, and algorithm development. Project efforts will center on the technical areas of sensor characterization and sensitivity analysis, target and sensor modeling, experiment and observation, and on-orbit data analysis. The primary focus during the first year was on the shortwave infrared (SWIR) grating sensor. Through analysis of test data, new high-order processing algorithms have been shown to be sensitive to subtle varying signals in both the spatial and temporal dimensions. In addition, a prototype grating sensor model has been developed that can simulate spectral dispersion in spatial data for use in evaluating target signatures and ultimately mission performance. In subsequent years, efforts will focus on stringent assessment of spectro-temporal signatures from both the visible prism and grating dispersive sensors and the polarized filters that are expected to both enhance current missions and address new missions. This is expected to be achieved primarily through forward modeling of unique spectral signatures as well as target-detection-and-extraction algorithm development from space-based data collections and simulated data.

Adaptive Automation for Supervisory Control of Streaming Sensors 151277

Year 2 of 3

Principal Investigator: J. H. Ganter

Project Purpose:

National intelligence and security depend on effective remote sensing, the acquisition of knowledge from a distance using instruments that transform energy into information. Sandia remote sensors include the Multispectral thermal imager (MTI) and synthetic aperture radar (SAR) aboard unmanned aerial vehicles (UAVs).

To improve the performance and utility of remote sensors, Sandia recently conducted studies of human-labor demands located downstream of the sensing instruments. In the ground processing stage, signal-processing algorithms running on large computing clusters detect signatures in noise and classify signatures into target categories. But there is a surprisingly large, and even growing, reliance on human experts to tune the algorithms to user needs, mission goals, and evolving situations. The next generation of sensors will change a labor shortage to a labor crisis. Manual labor has become the primary limiting factor in both technology rollout to national security missions and R&D investment in new sensors.

To solve the sensor labor crisis, we need a new analog to the autopilot that has become ubiquitous aboard aircraft and ships. This trusted and powerful machine aid will free human time and attention for tasks people do well. These skilled tasks include situational awareness, situational understanding, and the making of difficult choices among options. This project will invent a sensor autopilot by hybridizing methods from statistics, signal processing, control theory, and cognitive systems.

A sensor autopilot must solve problems that are underspecified and thus dramatically more difficult than typical control problems. Probability density functions (histograms) of both targets and backgrounds are noisy, unknown a priori, and evolving. Solutions must be numerically generated very rapidly to remain within the time constant of the sensor control loop. We believe that creatively blending adaptive signal processing with control theory, human-supervised training, and machine learning could solve many problems currently limited by human-operator bandwidth.

Phase Diversity for Advanced Systems 151278

Year 2 of 2

Principal Investigator: E. A. Shields

Project Purpose:

Due to limitations in manufacturing and alignment, all imaging systems exhibit an inherent amount of optical aberration, which degrades performance. For orbital systems, these quasi-static aberrations are compounded by misalignments induced by gravity release and dynamic thermal loads which cause changes to the structure, directly distort optical surfaces, and alter refractive characteristics of lenses. These combined effects can severely degrade imaging performance.

Sandia's current techniques for compensating for these effects on-orbit include piston actuation of mirrors and heating of lens groups to implement desired focal changes. These approaches are calibrated with star images (requiring periodic re-pointing), are susceptible to hardware failure, and exhibit limited utility in addressing aberrations other than defocus. Other approaches for correcting optical aberrations utilize wavefront-sensing techniques and actuated deformable mirrors. These architectures require a significant number of additional optics and greatly increase system complexity and risk.

Phase diversity (PD) is an image-processing technique that operates on a collection of defocused images of a specific scene. The ensemble of defocused images and known defocus values are used to reconstruct the unaberrated scene and the wavefront aberrations of the imaging system.

PD has successfully been applied to imaging systems with limited fields-of-view (FOV) over narrow spectral bands. Yet, theoretical development has not addressed issues of field-dependent aberrations inherent in systems with larger FOV. Algorithms that can accommodate wavelength-dependent aberrations in scenes with broad spectral content have also largely been ignored.

For broadband terrestrial imaging systems, aberration content across the FOV and spectral bandwidth can vary significantly. The effects of these aberrations are convolved in the collected panchromatic imagery, complicating the problem of separability and image recovery. An innovative approach to including these dependencies in the algorithm itself can enable application of PD image enhancement to wide-field earth surveillance missions.

Summary of Accomplishments:

We developed a theory for implementing phase-diverse phase retrieval for spectrally broad systems. This theory generalizes work previously done in this field. In our formalism, the wavefront content as a function of wavelength is allowed to vary in an unknown fashion. Furthermore, the spectral weights can be optimized as well.

Using this theory, the possibility of characterizing the spectrum of an unknown point source arises. One can first calibrate the system using a known point source to determine the wavefront variation as a function of wavelength. Once this is known, the system could be used to image an unknown point source, and the spectral weights could be optimized. By considering the known spectral response of the imaging system, the spectral content could be determined using a panchromatic imaging system.

We analyzed the effectiveness of this theory using both simulations and measured data. Simulations show that this algorithm is effective even when more wavelengths are included in the simulation than are used in the reconstruction, something critical for the algorithm to work with broadband systems.

Experimental testing demonstrated that this algorithm could effectively reconstruct wavefronts in a system with two lasers as the source, a stepping stone to experimentally verifying the algorithm on a true broadband source.

Future work should concentrate on improving the reconstructions for the two-wavelength configuration as well as experimental testing with a true broadband source.

This effort enabled Sandia to achieve a high level of experience with phase-diversity techniques. This program enabled a separate, program-funded effort geared towards developing phase-diversity techniques with undersampled optical systems. This effort demonstrated, for the first time, that phase-diversity imaging techniques can be used by undersampled imaging systems in a deployed environment. This effort will likely lead to other uses of phase diversity where interferometry is not feasible.

Significance:

The state of the art of phase-diversity techniques has been advanced by development of the broadband phase-diverse phase-retrieval algorithm. This theory allows phase-diversity techniques to be used for optical systems that traditional algorithms would have precluded.

Furthermore, this project has enabled a program-funded effort to study how phase-diversity techniques can be used with deployed remote-sensing systems. This has the potential to provide improved imagery from a host of national assets and a variety of other optical systems.

Lastly, this work has greatly enhanced the ability and visibility of computational optics techniques at Sandia.

Novel Signal Transmission and Intercept Methods using Applied Information Theory and COTS Radios

151283

Year 2 of 2

Principal Investigator: D. R. Fay

Project Purpose:

This project will create/apply novel methods of signaling for the purposes of "non-standard" communication, tagging, tracking, and locating (TTL). These methods will be applied to commercial off-the-shelf (COTS) radios to form an organic platform that can be used for these purposes. Leveraging commercial radios have obvious cost benefits and are available to assets worldwide. Each radio will exhibit unique challenges to modify its traditional output, and the modified functionality can range from packet structure, frequency, power to modulation, or any combination of these. We have demonstrated the novel, non-standard capabilities of these radios by getting them to successfully perform outside of their officially specified behaviors and radio frequency (RF) characteristics.

Summary of Accomplishments:

We have successfully developed methodologies, frameworks, and platforms for enabling non-standard behavior on COTS radios. We have tested and demonstrated the efficacy of these methodologies on both a PC platform as well as on a smartphone platform.

Significance:

By enabling COTS radio technologies to behave in non-standard ways, this project allows for the development of communications and tagging technologies at a lower cost and higher level of versatility.

Command Intent on the Future Battlefield: One-to-Many Unmanned System Control 151285

Year 2 of 3

Principal Investigator: S. Buerger

Project Purpose:

The DoD faces a looming crisis in the control of unmanned systems (UMS). Acquisition trends driven by Congressional mandates ensure that forces will continue to unman. Today's multiple-operator-per-vehicle remote-control methods will scale neither to meet the needs of a cost-conscious security establishment in which manpower is the single largest cost driver nor to accomplish effective, centrally commanded operations involving tens to hundreds of heterogeneous unmanned assets working together in the same battlespace. DoD leaders are recognizing that, in predominantly unmanned conflict, intelligent, coordinated, man-in-loop control of multiple UMS will be the key differentiating technology. Previous approaches to multiple-UMS control have worked toward an ideal of pure autonomy, but to adopt autonomous control systems for potentially lethal assets would require certain perfection in algorithms. Instead, we envision one-operator-to-many-asset control systems that capitalize on human superiority in perception, tactics, and strategy and that compensate for perpetual imperfection in control algorithms by keeping human commanders in total control in real-time while making teams of heterogeneous unmanned assets responsive to command intent.

This project is directed toward demonstrating several high-risk aspects of our long-term vision for predominately unmanned combat. A highly layered control architecture has been developed that enables the use of modular control alternatives. An efficient high-level task-assigning controller has been developed. Mid-level controls have been developed and implemented on unmanned ground vehicles to enable independent execution of behaviors including target following, line / area exploration, and obstacle avoidance. The architecture allows an operator to direct mission execution by manipulating and continually updating a single data packet that includes mission objectives and priorities. A user interface allows the operator to intuitively influence this packet. Upcoming work will focus on facilitating operations in more complex, more realistic environments. As a part of upcoming work, an aerial asset will be integrated and controlled as part of an air-ground team.

Multi-Mission Software-Defined RF Spectrum Processing

151286

Year 2 of 3

Principal Investigator: P. E. Sholander

Project Purpose:

The military's migration to network-centric warfare requires a robust set of airborne sensors that are directly taskable by unit commanders. For cost and complexity reasons, these sensors will be SWAP-constrained (Size, Weight and Power) and flown on unmanned aerial vehicles (UAVs). These multi-mission Unmanned Aerial Systems (UAS) will enable novel system-level applications and Concepts of Operations (CONOPS) via wideband “software-defined spectrum processing” (SDSP) that supports a range of surveillance (e.g., synthetic aperture radar [SAR]) and communications missions. For example, multiple cooperating SDSP-enabled UAS could improve communications within urban terrain and other challenging environments. They could also provide an organic high-data-rate link for SAR imagery download to a Ground control station (GCS) and thereby enable a flexible partitioning between airborne- and ground-based processing. An enhanced communications capability between UAS could enable multi-static SAR capabilities and the exchange of baseline change-detection data. More generally, a flexible SDSP system that could receive, digitize, and process 300-500 MHz chunks of spectrum while being swept (over several seconds) through the frequency range of several hundred MHz to several GHz would support a wide range of Sandia's missions. While wideband SDSP systems present significant computational and signal processing challenges, there are also significant challenges in the designs of the antennas, radio frequency (RF) front ends, and initial spectrum digitization.

This project will focus on SDSP hardware design and implementation and the novel CONOPS enabled by a multimission SDSP capability. A key goal is the ability to switch between those capabilities, in real-time, while maintaining a small-SWAP package. This capability will provide a significant technological advancement in the application of SAR systems that does not match any current programs under execution. The majority of current program customers are looking for incremental improvements for their already-defined mission space.

A Scalable Emulytics Platform for Observation of Windows-Centric Network Phenomena

151287

Year 2 of 3

Principal Investigator: C. T. Deccio

Project Purpose:

The purpose of the project is to create a system to understand both the behavior and the potential threat of distributed applications in large-scale networks comprised of Windows hosts. One challenge facing computer-security researchers is the lack of tools for understanding large-scale emergent behavior of Internet applications as run on their native operating system (OS) rather than simulated. There has been some success scaling large arrays of Linux-based virtual machines (VMs) for this purpose. Due to its large memory footprint, however, Windows is at a considerable disadvantage. The goal of the proposed work is to create ways to produce a scalable emulytics platform for Windows OSes where it will have more impact and value to network analysts and cybersecurity.

During the first year of the project, we focused on minimizing the footprint imposed by Windows so that we could maximize use of resources on hardware to launch a large number of virtual machines per physical host. We also demonstrated proof-of-concept work in networking the virtual machines together on a cluster of commodity machines built for this purpose. We ended up successfully launching 65,000 instances of Windows VMs in an isolated network, in which each subsequently downloaded and executed an application.

During the second year of the project, we began work on building custom networks resembling those deployed in real enterprises to enable a more accurate network architecture. We built a network of VMs resembling Sandia's network and began techniques for visualization to analyze behavior.

During the third and final year of the project, we plan to build on development from the previous years, gleaning lessons learned from proof-of-concept development to revamp our development and launch tools and returning to emulation of large-scale applications with visualization analysis.

Discriminative Feature-Rich Models for Syntax-Based Machine Translation

151373

Year 2 of 2

Principal Investigator: K. R. Dixon

Project Purpose:

In the past few years, automatic machine-translation (MT) systems have come a long way. These MT systems take text from a source language and attempt to generate text with the same meaning in a target language. While the performance of these systems is improving steadily, any user of MT systems knows that their performance still has a long way to go to reach the level of human translators. For years, standard MT systems have assumed that the features of the language-translation problem are localized to the words being decoded. While this assumption is obviously incorrect and virtually always violated in all languages of interest, MT systems assume feature locality to make the translation problem computationally and mathematically tractable. Recent advances using long-distance language features have created state-of-the-art performance gains for many tasks in natural language understanding, such as question answering and automatic summarization. However, these features have received scant attention from machine-translation researchers due to the mathematical complexity and computational burden of relaxing traditional local-feature assumptions. In collaboration with Carnegie Mellon University, we will improve the performance of MT systems by exploring theoretical and empirical effects of nonlocal features. As this is a relatively new area of research, we will first create various nonlocal, cross-language features to address frequent errors made by MT systems. With these nonlocal features in hand, we will develop novel translation algorithms based on violating the long-held local-feature assumption. Finally, we will analyze and demonstrate the performance of creating translation models using machine-learning techniques that exploit the nonlocal features.

Summary of Accomplishments:

Fully automated, high-quality machine translation promises to revolutionize human communication but still suffers from serious deficiencies. In this work, we addressed four areas in which we believe translation quality can be improved across a large number of language pairs.

The first relates to flexible tree-to-tree translation modeling. Building translation systems for many language pairs requires addressing a wide range of translation divergence phenomena. We described the first machine translation system based on quasi-synchronous grammar.

Secondly, we sought to unify disparate translation models. Specifically, we used rules that combine phrases and dependency syntax by developing a new formalism called quasi-synchronous phrase dependency grammar.

To build these models, we needed learning algorithms that could support feature-rich translation modeling. Due to characteristics of the translation problem, machine-learning algorithms change when adapted to machine translation. We developed novel variations on this loss, drew connections to several popular learning methods for machine translation, and developed algorithms for optimization. Our algorithms are effective in practice while remaining conceptually straightforward and easy to implement. In this research, we took the first steps in using unsupervised parsing for machine translation.

Significance:

Automated machine translation is an area that touches many areas of national security and is, therefore, germane to the operations of multiple federal agencies. Better translational systems, particularly those that appropriately handle idiomatic language, will have a transformative effect on the way our policy makers are able to make informed decisions. The work funded by this project has furthered the scientific frontiers in this critical area.

Relational Decision Making 151374

Year 2 of 3

Principal Investigator: L. E. Matzen

Project Purpose:

For most real-world decisions, almost any choice is possible, and there is a high degree of uncertainty associated with the outcome. Making decisions is a constructive process which requires: 1) binding together arbitrary collections of items, locations, and events to create a mental representation of the decision, 2) holding multiple scenarios online simultaneously, 3) comparing between these scenarios, 4) selecting the preferred scenario, and 5) planning and executing the behavior required to select that scenario. Understanding these computational processes which undergird decision making is a considerable technical challenge and fruitful area of research. Most previous decision-making research focused on closed-set decision making: choosing within a small, known menu of possible options. The goal of the relational decision-making project is to break away from studies of simple choices, and instead focus on how the brain constructs and compares alternative scenarios constructed from configurations of items. Previous research has implicated the medial temporal lobe of the brain, and specifically the hippocampus, in binding together arbitrary, accidental, and heterogeneous relations between stimuli to support both declarative memory and online representation. The first year of work has produced intriguing modeling results and empirical data which directly pertain to how people mentally construct and reconstruct events online. The next year builds upon this success by synthesizing and extending the findings. The modeling half of the project will extend the nonlinear dynamic hippocampal model to capture and reconstruct more complex configurations of stimuli, better mirroring the complex relational configurations present in the empirical data. These two techniques help elucidate how the relational memory representations constructed by the hippocampus form a guide for decision making. The constraints produced by these representations often result in improved performance, but sometimes representational constraints can result in systematic decision-making errors. This work is in collaboration with University of Illinois at Urbana-Champaign.

Supervised Reconstruction and Recognition for Nonlinear Corruption 153891

Year 2 of 2

Principal Investigator: H. Anderson

Project Purpose:

The purpose of this project is to develop supervised learning methods to handle signals and images that have been corrupted in a nonlinear, difficult-to-model manner. Signal and image analysis is often hampered because the signal of interest is corrupted in a way that is difficult to model. Mathematically convenient corruption models (e.g., linear and time invariant blur with additive noise) inadequately describe the physical corruption phenomena present in these systems.

As an alternative to modeling the corruption explicitly, we propose the use of uncorrupted and corrupted signal examples as a means to characterize the corruption, estimate (reconstruct) a signal from a corrupted signal, and classify the corrupted signal. Related work in blind deconvolution, joint deconvolution and classification, and dataset shift mitigation have focused on simple statistical or linear models that are not true to the observed data for applications of multispectral and scanning-electron-microscopy (SEM) imaging considered here. In contrast, this work aims to use data-driven, non-parametric models for restoration and recognition.

We will address two problem areas: 1) early classification of time-series profiles that have been corrupted by a nonlinear mechanism with unknown parameters and 2) early detection of image artifacts caused by unpredictable mechanisms. This work may benefit numerous existing and future applications in remote sensing, microscopy, and digital forensics that exhibit nonlinear degradation but where example images and signals are readily available.

Summary of Accomplishments:

We developed a framework where both “clean” and “corrupted” training signals are utilized to grossly characterize nonlinear warping. In particular, we focused on methods that leverage training data to mitigate missing data, time warping, and enable early classification.

We developed early classification methods that exhibit superior performance when compared to recently published methods operating on open benchmark time-series datasets. The contribution includes the introduction of ‘reliable’ early classification, wherein a user-specified reliability parameter provides a theoretical and computationally efficient guarantee that the early classification decision agrees with the final decision with specified probability.

We also tested subspace approximation methods — principal-component analysis and dictionary learning, in particular — as a way to characterize “normal” signals and detect “anomalous” signals. This was applied to image-anomaly detection by learning “normal” image patterns from overlapping image patches and to detection nonlinear corruption by coding complexity in the subspace projection.

Significance:

This research provides S&T advancement in time-series classification, providing much-needed reliability guarantees. The approach may be applied to DOE mission areas, for example, as it applies to early classification of proliferation events, or for image recognition tasks in the information operations area.

Thin Magnetic-Conductor Substrate for Placement-Immune, Electrically Small Antennas

154259

Year 2 of 2

Principal Investigator: T. W. Eubanks

Project Purpose:

An antenna is considered to be placement-immune when the antenna operates effectively regardless of where it is placed. Placement immunity is hard to achieve for antennas due to the impedance-changing effects of the environment on antennas.

By building antennas on magnetic-conductor materials, the radiated fields will be positively reinforced in the desired radiation direction instead of being negatively affected by the environment. Although this idea has been discussed thoroughly in theoretical research, the difficulty in building thin magnetic-conductor materials necessary for in-phase field reflections prevent this technology from becoming more widespread.

This project proposed to build and measure an antenna on a new type of non-metallic, thin magnetic conductor. This measurement would demonstrate the antenna's placement-immunity by showing that the antenna would continue to function effectively when placed near water or metal materials that usually detune the antenna. This problem had not been previously addressed because non-metallic, thin magnetic-conductor materials had not yet been discovered.

Summary of Accomplishments:

We invented, fabricated, and measured a ceramic rod-based artificial magnetic conductor that makes an antenna above it placement-immune with regards to the antenna's resonant frequency and gain performance in free space.

We discovered a measurement method suitable for determining the dielectric constant of materials with dielectric constants higher than 1000, and we measured the dielectric constant of the material used in our artificial magnetic conductor at several frequencies.

We designed, fabricated, and measured tunable half-wave dipole antennas that were used for characterizing the performance of the artificial magnetic conductor.

Significance:

By pioneering ceramic-based artificial magnetic-conductor substrate design for placement-immune antennas, we have given Sandia a tool to leverage when creating rapid placement antenna systems in remote locations.

We have also created a new field of antenna science that combines radio frequency and ceramics engineering. Radio-frequency engineering tools are required to analyze the electric and magnetic fields shared among the ceramic pucks, and ceramics engineering tools are required to make the ceramic pucks uniformly with known properties. This work has potential relevance to missions of both DoD and DHS.

Simplifying Virtual-Machine Security through Foundational Introspection Capabilities

154320

Year 2 of 2

Principal Investigator: B. Payne

Project Purpose:

Ensuring the security of a computer system requires the careful integration of many components. Key among these is security monitoring. Recent research trends show an increasing acceptance of external host-based monitoring techniques such as virtual-machine introspection (VMI), a technique for viewing the runtime state of a virtual machine (VM). VMI's primary drawback, known as the semantic-gap problem, is that it requires significant semantic knowledge and is error-prone due to its low-level nature.

Solving the semantic-gap problem is hard because it requires encoding a complete understanding of the target system such that a monitoring program can readily access it. As a result of this overwhelming challenge, most VMI-developers have created "one-off" solutions. This typically involves determining the information needed about the target system (e.g., through reverse engineering or program analysis) and then 'hard-coding' it into a VMI-based program such that the monitoring functionality works in that program but is difficult to use in other related programs.

We propose to address this problem by providing a framework for integrating the "one-off" solutions into a database of semantic knowledge. Using this database, we propose to enable VMI-based programming at a higher semantic level that is less error-prone. The key research components of this proposal include:

- A programming language and/or high-performance runtime that allows VMI-based application developers to access data and execute key algorithms from the target software using high-level symbolic semantics that are familiar to the developers.
- A collection of program analysis techniques for extracting semantic information from software, vendor symbols, raw memory, and other key sources of information.
- A runtime and/or compiler that provide automated handling of error conditions that are common in VMI programming but uncommon in other settings in order to simplify VMI-based application development.
- Tight integration of each component described above with a VMI library.

Summary of Accomplishments:

We created LibVMI, a virtual-machine introspection library based on the related XenAccess library. In addition, we provided integration between LibVMI and Volatility, a forensic memory analysis framework, to drastically simplify the creation of VMI applications. LibVMI provides a useful application-programming interface (API) for reading to and writing from a virtual machine's memory. It also provides a variety of utility functions that are useful to VMI developers. All of this functionality works for VMs running under either of the two most popular open-source virtualization platforms: Xen and KVM. LibVMI programs can also use a static memory snapshot as a data source. This flexibility allows developers to create VMI applications once and have them work in each of these settings without modification. We wrote an address-space plugin for Volatility that enabled using LibVMI for memory access. Since Volatility is written in Python, this required also writing a Python wrapper for the LibVMI API. With this functionality in place, one can easily write new VMI applications using Volatility.

The key areas of improvement for LibVMI under this project include:

- Refactoring the code to support KVM, and to make supporting other virtualization platforms very simple.
- Improving the API to greatly simplify VMI development. Specifically, replace manual memory mapping with read and write functions that behave as expected to a POSIX developer.
- Improving the overall performance of the library.
- Adding support for 64-bit VM guest operating systems.
- Adding the PyVMI wrapper library.
- Improving Volatility integration.
- Fixing a variety of bugs ranging from correctness to memory leaks.

Significance:

The successful completion of this work helps to push VMI into the mainstream. This foundational capability can then be leveraged to solve some of the most challenging computer security problems that we, as a community, face today. Some of the problems where VMI could play an integral role in the solution include secure operating systems, information provenance, malware detection and mitigation, fault-tolerant systems, provably secure systems, insider threat, forensics, and attack attribution. By developing better VMI capabilities at Sandia, we will be well positioned to participate in the solution to many of these key security problems.

Leveraging Safety Applications for Global Revocation and Congestion Control in Vehicular ad hoc Networks

155408

Year 2 of 3

Principal Investigator: J. J. Haas

Project Purpose:

Wireless networking enables communication among highly mobile entities in many different arenas. Unmanned aerial vehicles (UAVs), soldiers, and ground vehicles form tactical or disaster relief mobile ad hoc networks (MANETs). Civilian vehicles will form vehicular ad hoc networks (VANETs) to improve vehicular safety. These two networks have widely different goals but have similar foundations in terms of security functionality; network participants should be authorized to use the network by a trusted authority, and participants that are deemed untrustworthy should have their authorization credentials revoked to limit the amount of damage they can do. In both MANETs and VANETs, contact with trusted nodes may be limited due to funding constraints and the extensive network coverage.

A trusted authority (TA) will be unable to observe events that should lead to participants' revocations. Thus, revocable offenses need to be detected in a distributed manner by the untrusted nodes. Such offenses should be reported to the TA opportunistically so that the TA can revoke the offenders' credentials and distribute information such that all nodes can identify the offenders. This process is referred to as global revocation and is an open research problem, which will be addressed.

MANETs or VANETs conditions (e.g., density, wireless channel) vary widely due to nodes' mobility, and thus require congestion-control mechanisms to adapt. However, since congestion-control mechanisms affect network connectivity and quality of service, secure congestion-control mechanisms that minimize, limit, or eliminate the influence attackers have on those mechanisms or properties will be investigated and designed.

The US Department of Transportation plans to mandate in 2013 future VANET capabilities in vehicles. Global revocation is a vital piece of VANET security systems, without which VANET systems will not have a means of feedback to remove revocable entities. Congestion control may be necessary for increased safety-application effectiveness. Attacks on insecure congestion-control algorithms may reduce safety-application effectiveness.

Identifying Dynamic Patterns in Network Traffic to Predict and Mitigate Cyberattacks

155799

Year 2 of 3

Principal Investigator: J. D. Wendt

Project Purpose:

The purpose of this project is to improve cyber defenses against social engineering attacks. For attackers to craft personalized phishing (spear phishing) attacks, targeted web-based research, including research regarding Sandia web sites, will occur to identify appropriate targets. In this project, we work to visualize and analyze visit patterns to our web pages that may signal such pending attacks.

Noteworthy scientific and technical accomplishments over the lifetime of the project include development of tools to collect and store the data necessary for the analysis of visit patterns, demonstration-quality visualizations that provide new ways for analysts to look at web-server logs, and early statistical analytics for deriving additional data on visitors based on their server traffic.

The key R&D accomplishments have implications for the general S&T community and the national security mission areas. Spear phishing has shown itself to be quite effective at introducing malicious software that bypasses conventional cybersecurity systems; this work is creating new defenses against these tactics.

Alternative Waveforms for New Capabilities in Radar Systems 155802

Year 2 of 3

Principal Investigator: R. M. Naething

Project Purpose:

Synthetic-aperture-radar (SAR) imaging systems achieve high resolution in range by transmitting very-high-bandwidth waveforms. The radar's high-bandwidth channel can also be used to transmit and receive information at very high data rates. The principal goal of this work is to research and develop means of allowing existing radar hardware to perform communications.

This year, we developed several novel algorithms that enabled new features for our radar systems. These algorithms provided a significant performance benefit over the previous state of the art and will enable new modes and capabilities for Sandia's SAR imaging systems.

Improving Shallow Tunnel Detection from Surface Seismic Methods 156137

Year 2 of 3

Principal Investigator: N. Bonal

Project Purpose:

The purpose of this project is to understand the effects that tunnel construction has on seismic waves and to improve detection and location of clandestine tunnels and/or underground facilities using seismic methods. Seismic reflection and refraction have been viewed as some of the better methods to detect tunnels, but results have been good in some cases but not in others. A recent study of competent rock shows that the largest responses from the tunnel are not reflections or refractions. Additionally, the damaged zone, fractures created/enlarged by tunnel construction, has a negligible effect on reflected and refracted seismic waves in competent rock. However, clandestine tunnels in the near surface are often constructed in weak rock and near the water table, where pore spaces around the tunnel dry out. These effects may have a significant impact on seismic waves and should be investigated. Also, signal-processing techniques other than seismic reflection and refraction should be developed for tunnel detection. The goals of this project are to: 1) determine the effects, if any, that changes in rock properties of the tunnel-damaged zone (e.g., material fracturing and pore dewatering) in the near-surface have on seismic waves and 2) increase tunnel-detection ability by improving signal-processing techniques, including reverse time migration (RTM) and surface-wave diffraction. This project aims to accurately model the area around the tunnel-damaged zone, which has been created by the tunnel's construction. Previous studies do not address the effects of dewatering or construction in weak, poorly consolidated materials near the surface, which may be significant. Modeling seismic-wave propagation through the tunnel-damaged zone will demonstrate whether it has a significant effect on seismic velocities. The proposed work will utilize preexisting data from near-surface clandestine tunnels to compare modeling results and test processing techniques.

Silicon Photonics for Ultra-Linear RF Photonic Devices and Links 157633

Year 2 of 3

Principal Investigator: C. Derosé

Project Purpose:

The purpose of this project is to develop a silicon-based platform for advanced radio-frequency (RF) photonics. Silicon offers the flexibility to do both chip and wafer scale integration with high-speed RF and digital electronics. The addition of RF photonic functionality to the platform will create the possibility of making revolutionary improvements in systems, which are important to the national security mission.

During this project, we will demonstrate several best-in-class device technologies on a silicon-based photonic platform, including highly linear optical modulators, high-power photodetectors, and tunable RF photonic filters. Upon the successful completion of this project, we will have developed a platform for system-level research that will impact the national security mission.

Integrated Autocatalytic Composite Strategies

158518

Year 2 of 2

Principal Investigator: J. Carroll

Project Purpose:

Polymeric composites that autonomously respond to external stimuli provide a wealth of novel engineered solutions (e.g., self-healing polymers for structural and aeronautical applications). In this mechanical embodiment, microencapsulation techniques enable compartmentalization of reactive components (i.e., resins and curing agents). When the matrix is subject to structural damage, the capsules rupture and polymerize within the crack, thus restoring mechanical integrity (i.e., self-healing). However, to date, no one has identified a methodology for an electrical analog that results in high-quality radio-frequency (RF) conductive traces. It is the intent of the proposed work to demonstrate the feasibility of polymeric composites that respond to external stimuli by autonomously initiating an electroless metallization reaction, resulting in conductive traces for enhanced application functionality.

“Electroless plating” is a time-tested, room temperature, chemical reduction process wherein a metallization reaction proceeds spontaneously on select surfaces. This plating process provides a means to produce uniform coatings on a wide array of substrates for mechanical and electrical applications. The versatility and cost effectiveness of this process has resulted in widespread use throughout the industrial sector, but the underlying process is overly limited. The reduction reaction only initiates when a substrate is physically submerged into a solution bath containing the reducing agent. We propose, through compartmentalization and embedding of plating reactants in a flexible composite, a new innovative sensor technology will be realized (via an autonomous response mechanism). Thus, the initial insulating reactants proceed to form conductive traces upon rupturing within the polymer matrix. Since the reactant microcapsules are dispersed initially throughout the liquid matrix, several form factors can be envisioned for key intelligence, surveillance, and reconnaissance applications (e.g., coatings on structurally complex surfaces/substrates).

Summary of Accomplishments:

To date, self-healing material systems have largely focused on restoration of mechanical properties of structural composites; however, the self-healing concept based upon the release of liquid content from microcapsules is a generic process adaptable to many other functionalities, such as restoration of electrical conductivity. Such a mechanism has been explored and verified by a charge-transfer salt process generated from two precursor solutions. This two-part chemistry enables electronic self-healing via two liquid-filled microcapsules that mix upon rupturing and form a conductive compound. Rapid and spontaneous generation of a conductive path via microcapsule delivery enables autonomous conductivity. The solutions were individually incorporated into microcapsules as solutions in phenyl acetate (PA), resulting in particle sizes of approximately 50 to 100 microns. Upon crushing via mortar and pestle, DC conductivities were experimentally measured to be on the order of 5 S/cm.

Significance:

Thermomechanical failure of conductive traces in highly integrated circuits results in loss of function that is often impossible to repair and remains a long-standing problem hindering advanced electronic packaging. Autonomous healing of an electrical circuit with nearly full recovery of conductance post-damage would enable more sustainable electronic devices with increased fault tolerance, improved circuit reliability, and extended service life; this is relevant to national security missions of DoD, NNSA, and other agencies.

A High-Voltage, High-Current Thyristor Stack Command-Triggered by dV/dt — An Improved MOS-Controlled Thyristor-Like Nanosecond-Closing Switch

158698

Year 2 of 3

Principal Investigator: R. J. Focia

Project Purpose:

The metal-oxide-semiconductor (MOS) metal-controlled thyristor (MCT) currently used as the closing switch in solid-state firesets has exhibited failures on the bench and in the field during pre-shot safety checks. The cause for the failures is unknown, and manufacturer support on the failure issues has been limited at best. The MCT consists of thousands of cells switched in parallel and is currently available from only a single source. Although the MCT has higher time-rate-of-change of current (di/dt) capability than ordinary thyristors, switching thousands of devices in parallel can be problematic and a single-source supply of devices could be detrimental to the long-term success of a product. The challenge in this effort will be to fabricate a hybrid solid-state closing switch with voltage hold-off and current-handling capabilities equal to or better than that of the MCT but with a higher di/dt capability and improved reliability. Proof of concept of the new three-terminal solid-state closing switch will be accomplished by fabricating the hybrid switch by monolithic integration of commercially available thyristor and diode chips, metal-oxide-semiconductor field-effect transistor (MOSFET) switches, and a minimum number of passive components.

The potential outcome of this research and development effort is a new, command-triggerable high-power solid-state closing switch for use in pulsed-power applications. We intend to creatively exploit a known effect in thyristor structures in order to provide a solid state closing switch capable of high hold-off voltages, nanosecond or faster closing times, low jitter, and high pulsed currents. Although proof of concept will be demonstrated using a monolithically integrated device, we also propose to design, model, and conceptualize a fabrication process for an entirely new multi-junction thyristor-like structure. The new closing switch will have wide application in the pulsed power community.

Explosives Detection with Neutrons from a Short-Pulse High-Intensity Neutron Source

158700

Year 2 of 3

Principal Investigator: O. Doron

Project Purpose:

This project investigates the use of a short-pulse high-intensity neutron (SPIN) interrogation source coupled with neutron and gamma ray sensors to find buried explosives. The approach promises a powerful new method to locate buried explosives, such as landmines and unexploded ordinance, deeper in the ground, faster, and more accurately than is possible with current methods. The current searching depth and time to find objects with active neutron interrogation technologies is relatively shallow due to two limiting factors: the intensity and duration of the neutron pulse from a neutron generator (NG) and the poor signal-to-noise ratios (S/N). Traditionally, finding explosives in a large area requires many neutrons and a high S/N. However, it is difficult to achieve both of these requirements because, as the production rate from an NG increases, the S/N decreases.

Preliminary data for SPIN interrogation of materials shows that it may provide capabilities that require two orders-of-magnitude fewer neutrons and 100 times shorter sample time than state-of-the-art systems, including the associated particle technique (APT). The NG that we plan to use for this work has a pulse width in the 10-nanosecond range versus the microsecond range, which is standard for NGs. The narrow width of the pulse in the proposed NG is advantageous in several different ways, including the increase of S/N; with technology advancements and narrower pulse widths, time of flight (TOF) measurements will be possible as well. Currently, an APT NG can provide sub-nanosecond TOF timing resolution. The neutron and gamma ray detectors that are being proposed for use are highly sensitive and selective for either neutron or gamma rays. The combination of the NG and detectors that will be used for the system will also increase the sampling depth and the probability of locating explosives.

An Adaptive Web Spider for Multi-Modal Data 158747

Year 1 of 3

Principal Investigator: J. T. McClain

Project Purpose:

While search capabilities are improving with an increased number of utilities to locate documents and images on the Internet, the task to locate data continues to be manually intensive and relies on astute search abilities. Quickly and accurately locating information is most successful when the user has a priori knowledge about the relevant search terms and domain areas. Typically, the process to locate a document involves iteratively examining the URLs and web pages returned and modifying key terms to hone the search. Searching for images is limited to the metadata a person has associated with the image, and not the image itself. We propose to develop an intelligent web spider (a.k.a., crawler) to automate human search and browsing behavior on the Internet to significantly improve the speed, accuracy, and the comprehensiveness of an Internet search. Such a capability will accelerate the data gathering tasks, thus accelerating the intended information processing, review, or analysis objective.

Acknowledging the value of data content inherent to a picture and the value of the implications of recent advancements in data comparison for text and images is at the core of this innovative project idea. We propose to develop an intelligent web spider with the capability to examine both text and images within a web page or document, as well as the capability to adapt its search strategy using machine learning algorithms. If successful, this automated search capability will allow for more efficient, more accurate, and more comprehensive search results with minimal user intervention. The potential benefit can encompass Internet users across all domains: government, academia, and private industry.

Vulnerability Analysis of Long-Term-Evolution-Capable Devices

158748

Year 1 of 2

Principal Investigator: J. R. Ford

Project Purpose:

This project seeks to develop methods for utilizing digital signal processors (DSPs) to accelerate software-defined-radio (SDR) applications within the open source GNU Radio framework. The chief advantage of SDR is the ability to rapidly develop new wireless receivers and transmitters; however, this flexibility is traded against lower efficiency. This reduced efficiency typically results in the need for more computational capability, which in turn requires more power, generates more heat, and occupies more volume. As a result SDR has made limited inroads into power and/or space constrained applications. In contrast to a general-purpose processor (GPP), DSPs are very well suited to the kind of processing required for SDR. Most users of DSPs tend to focus on one-off solutions or fixed applications rather than seeking flexibility. In FY 2012, this project demonstrated for the first time a DSP running SDR code within the GNU Radio framework with similar performance to a typical Intel-class computer when running at comparable sample rates. This accomplishment opens the door to investigating applications where DSP acceleration will provide substantial benefit to existing SDR implementations or enable new SDR capabilities that were previously difficult or impossible on GPPs, such as implementing a fourth generation long-term-evolution base-station GNU Radio.

System-Level Cyber Analysis of Cellular-Network Infrastructure 158749

Year 1 of 2

Principal Investigator: B. P. Van Leeuwen

Project Purpose:

The purpose of the project is to create a smartphone/cellular communications system cyber-analysis capability and research platform to include infrastructure representation. The developments will help address security problems in the cellular infrastructure and provide a capability to devise and analysis security solutions.

Cellular networks play increasing role supporting critical government and private information systems. Increased capability and ubiquity of mobile devices (smartphones) is resulting in increasing cyber exploit developments targeting the smartphone and increasingly targeting the cellular infrastructure. We will advance the state of the art in cybersecurity of the cellular infrastructure.

Key factors driving the adoption of smartphones by government agencies (e.g., DHS, FEMA, National Guard, and Army) are increasing functionality (e.g., beyond voice and texting), processing power and capability of the mobile platforms, and an increasing capability of the cellular infrastructure for data transport. With the increased infrastructure capability comes greater opportunity for cyber exploits resulting from Smartphone operating systems (e.g., Android, iPhone IOS) to manage resources, support a wealth of applications, and manage network connectivity to the cellular infrastructure. Both the infrastructure and smartphone OSES are vulnerable to cyber exploit via network connectivity. Classical tactics, procedures, and tools, including botnets and rootkits, used to exploit fixed computer networks are being reemployed to target smartphones. Infrastructure cyber-analysis methods and research platforms to assess impacts of cyber exploitation and to assess security measures are far from being satisfied.

Research to date assesses smartphone hardware and operating system for vulnerabilities and mitigation approaches while ignoring smartphone interaction with infrastructure. Infrastructure elements represent an important avenue for attack detection and mitigation because they control and manage connectivity. Our research is resulting in an analysis capability and research platform that enable analysis of exploit impact on cellular infrastructure.

The infrastructure research platform will utilize cellular infrastructure models, emulation, and real hardware. Sandia has experience with hybrid research-platform capabilities that enable combining domains into a single experiment (live-virtual-constructive capability).

An Approach to Predicting the Performance of Advanced Concretes using Peridynamic Theory

158750

Year 1 of 1

Principal Investigator: P. N. Demmie

Project Purpose:

Ultra-high performance concrete (UHPC) is increasingly being used in construction, and technology to predict its performance under loading needs to be developed. The goal of this project is to establish the viability of peridynamic theory to accurately predict the performance and fracture characteristics of UHPC.

Summary of Accomplishments:

We established the viability of peridynamic theory (PD) to accurately predict fracture characteristics of UHPC. A major accomplishment was the representation of the fiber content of UHPC at the continuum scale.

Significance:

This research significantly improves our ability to analyze the performance and predict the fracture characteristics of UHPC under loading using PD. The superiority of PD for predicting mechanical deformation with fractures constitutes an enabling technology in alignment with missions of both DOE and DHS.

PLC Backplane Analyzer for Field Forensics and Intrusion Detection 158752

Year 1 of 2

Principal Investigator: J. Mulder

Project Purpose:

The purpose of the project is to develop a system for detecting anomalies in backplane traffic of programmable logic controllers. Programmable logic controllers (PLCs) are embedded devices within control systems that are used to operate much of the US critical infrastructure (power plants, refineries, factories, rail transportation, etc.). PLCs are important due to their prevalence, their proximity to the physical system being controlled, and the lack of detection, protection, or forensics work conducted to characterize them.

Modular PLCs are composed of discrete components connected by a backplane. Our earlier work developed a proof-of-concept backplane forensics tool that can capture bus traffic for two popular brands of PLC.

We propose development of a more advanced backplane analysis system to examine communication between PLC modules. This analyzer will enable field forensics on PLCs, firewalling of certain behavior, and anomaly detection. We will explore technology transfer options either within the government or to industry partners.

Attacks on control systems have focused on network communications, Windows PCs, and PLC logic. We have not yet observed any attacks on PLCs at the hardware or firmware level.

We are proposing a level of introspection that is far beyond any existing security tools for control systems. Unlike most security products (e.g., firewalls, antivirus, intrusion detection system [IDS], etc.), this is not a reactive approach to existing vulnerabilities but a proactive effort.

Analyzing backplane traffic will allow for the detection of any attack, which changes the behavior of a PLC. The final product would address the problem of low-frequency/high-impact attacks by sophisticated adversaries using new/novel attacks against PLCs.

SAR and Multispectral SWaP Reduction via Compressive Sensing

158753

Year 1 of 2

Principal Investigator: D. Thompson

Project Purpose:

Air- and space-borne sensing platforms are designed to collect data of increasingly greater sophistication while reducing size, weight and power (SWaP) requirements. Compressive sensing (CS) is a new sampling theory that offers a unique design paradigm to reduce SWaP; it allows imaging from dramatically fewer measurements than traditional sampling. CS theory opens up new design concepts not possible with traditional paradigms. For example, a recent upgrade of the European Space Agency (ESA) Herschel/PACS (photodetector array camera and spectrometer) instrument applied CS in order to reduce onboard computational burden, to decouple onboard compression from on-ground image reconstruction, and to produce novel image products enabled by the unique characteristics of CS measurements. While the benefits of CS have been studied in many problem domains, its rigorous application to aerospace sensing platforms for national security missions is still nascent.

In this year of research, we have begun to investigate how CS may reduce SWaP requirements for air and space platforms, with an emphasis on CS for synthetic aperture radar (SAR) images, and for multispectral images. For multispectral imagery, we have demonstrated asymmetric compression/decompression and shown that it compares favorably to other methods studied recently in another project. We have demonstrated a proof of concept for compressive background removal in multispectral imagery and have tested the performance of target detection with varying levels of measurement compression.

For SAR, we have collected one of the first-ever real datasets of compressive phase histories to use in our experiments. We have demonstrated good results in reconstruction of SAR imagery from data undersampled by a factor of 2 and of ground-moving-target-indicator (GMTI) range/Doppler maps from data undersampled by factors of up to 10 and 20. We have further reconstructed SAR imagery and GMTI range/Doppler maps from the same compressive phase histories. Next year, we will improve processing time and attempt to approach near real-time.

Cueing for Change Detection via Geospatial-Temporal Semantic Graphs 158760

Year 1 of 1

Principal Investigator: J. Watson

Project Purpose:

The vast majority of static and video aerial data from DoD sources is unattended. Even when incoming data is actively observed by an analyst, the interaction is manually intensive and potentially error-prone; the analyst is looking for specific patterns of interest and accomplishes this by explicitly searching through data frames. Many of these patterns of life can be phrased in terms of change detection (e.g., identifying specific types of motion in video data) or the appearance of particular types of facilities in periodic wide-area data frames.

Ideally, automated methods for change detection would be deployed in conjunction with associated sensors to rapidly cue human analysts to specific data segments and/or regions within a given image for further expert investigation. Unfortunately, this ideal has not yet been materialized in practice. Pixel-based change-detection methods currently dominate the algorithmic landscape. However, these algorithms are notoriously sensitive to noise, including time of year, lighting, and sensor orientation. End results include false-positive rates too large to effectively cue analysts, or situations in which the signature or pattern of interest is statistically indistinguishable from normal background patterns.

We propose to leverage and extend our prior work using geospatial semantic graph technology to automatically identify complex targets in unattended data sources. We assume input data pixels have been pre-classified into various classes used to construct polygons representing primitive objects. Primitive objects become nodes in a semantic graph, while geospatial relationships become edges. Analysts can specify sub-graphs representing facilities of interest. Given such templates, sub-graph isomorphism algorithms identify matches, which are reported to analysts for further investigation.

We propose to extend our methodology to target cueing for change detection. We will semantically encode temporal and geospatial relationships between primitive objects and will automatically reason about those relationships. Where available, we will incorporate textual and non-image sensor information, as such sources can significantly aid detection of patterns-of-life activity.

Summary of Accomplishments:

The focus of this work was on conceptual design of a semantic-graph representation including temporal information and initial application of semantic-graph techniques to synthetic-aperture-radar (SAR) data.

For the conceptual design, we considered initial approaches that employ a full geospatial semantic graph for each time slice and then designed an improved approach that constructs graph elements only where significant change occurs.

We developed algorithms to identify basic ground-cover types corresponding to static features in SAR data. We measured the resulting recognition accuracy, including both producer's accuracy and user's accuracy. The recognition algorithms provide initial feature-detection capability, but substantial improvement is still required.

Using the features found in the SAR data analysis, we constructed geospatial semantic graphs and demonstrated search for simple feature ensembles. The graph search was successful, but overall search performance was limited by recognition capability.

We concluded with several important lessons learned, including the benefit of combining basic SAR feature recognition with other data sources.

Significance:

Large data streams are difficult for humans to analyze, particularly when features are difficult to recognize and/or patterns must be recognized from multiple data sets collected at multiple times. This work takes a step toward creating new data-processing systems that find these patterns, alleviating tedium for human operators and reducing the likelihood of errors of omission.

While this approach holds significant promise for achieving these improvements, the current results do not meet the ultimate requirements. Improvement in feature recognition is required; several detailed options are suggested in the final report. Implementation of the proposed temporal analysis is also required for better performance. For improved SAR performance, this work is of relevance to DoD missions.

Training Adaptive Decision Making

158764

Year 1 of 3

Principal Investigator: R. G. Abbott

Project Purpose:

Military personnel must make consequential decisions in complex situations where the outcomes of alternative actions cannot be anticipated with confidence, and changing circumstances may cause a good decision today to become a bad decision tomorrow. A recent Army Research Institute report stated, “The development of adaptive leaders has become a high priority for the Army; however, current research and practice related to adaptability is still in its infancy.” The Army has made corresponding commitments, such as the Adaptive Thinking and Leadership Course, a half-week component of the Special Forces Qualifications Course. Nevertheless, adaptive decision making remains an ill-defined concept, with little certainty of what makes decisions more or less adaptive. Without a scientifically grounded, principles-based approach for engineering training solutions, military leaders must rely upon thoughtful intentions, and some measure of faith, that their solutions are producing the desired outcomes (i.e., personnel capable of making effective decisions despite ambiguous, continually changing conditions).

Sandia’s R&D addressing cognitive elements of training has focused on After-Action Review (AAR). While valuable, AAR is inherently a retrospective approach with inherent limitations. There is a need to expand the scope of these capabilities to include all phases of training, beginning with instructional design. A recent Sandia project undertook a series of experiments to identify the factors that underlie effective adaptive decision making. While the resulting model has accurately predicted behavior for laboratory tasks, further research is necessary to translate these findings into technologies ready for operational settings. This project provides the essential bridge to convert scientific accomplishments into operational impacts. If successful, adaptive decision making will be transformed from a nebulous, yet important, concept into a formally defined, measurable attribute of individuals and teams. Furthermore, a scientifically-grounded foundation will emerge for engineering training technologies that assess the effectiveness of adaptive decision making, provide relevant performance feedback, and manipulate training content to improve decision-making performance.

A Complexity Science-Based Framework for Global Joint Operations Analysis to Support Force Projection

158765

Year 1 of 3

Principal Investigator: C. R. Lawton

Project Purpose:

The national defense enterprise constitutes a complex adaptive system-of-systems (CASoS) which coordinates the acquisition, planning, development, and deployment of national assets to accomplish effective global force projection. The military is undergoing a significant transformation as it modernizes for the information age and adapts to include an emerging asymmetric threat beyond traditional cold-war-era adversaries. This current and future operating environment will require us to cast global force projection in the broader context of a CASoS. The DoD must coordinate countless factors over a short period of time, including civilian leadership objectives, budget limitations, and adaptive adversaries, to determine the optimal trade-offs of resources and capabilities to accomplish national security missions.

Management of this dynamic constrained system has for decades relied on theory and best practices of public policy and procurement to maximize force projection. Techniques such as traditional large-scale, joint-services war gaming analysis is no longer adequate to support program evaluation activities and mission planning analysis at the enterprise level because the operating environment is evolving too quickly. New analytical capabilities are necessary to address modernization of the DoD enterprise. This presents significant opportunity to Sandia in supporting the nation at this transformational enterprise scale. Although Sandia has significant experience with engineering system-of-systems (SoS) and CASoS, we must invest in the fundamental research required to develop a modeling, simulation, and analysis framework to support enterprise-scale analysis.

We propose to develop an enterprise-modeling framework, which will leverage Sandia's capabilities in DoD SoS and CASoS modeling and engineering for capability analysis and design of alternatives. This framework and constituent modeling objects will push the science of large-scale modeling and simulation, distributed/parallel computing/simulation, high performance computing, uncertainty quantification, and large scale optimization techniques.

Validating Agent-Based Models through Virtual Worlds 158766

Year 1 of 2

Principal Investigator: J. Whetzel

Project Purpose:

Complex systems are of interest to the scientific community due to their ubiquity and diversity in daily life. Popularity notwithstanding, the analysis of complex systems remains a difficult task due to the problems in capturing high-volume data. Virtual worlds have recently emerged as a tractable way to analyze complex system interactions because these virtual environments are able to capture a great amount of data and at high fidelity, often tracking the actions of many individuals at a time resolution of seconds. Virtual worlds have been used to study phenomena such as social networks and financial systems; our focus is to identify behaviors related to large-scale conflict (LSC).

This project studies how one particular virtual world, a browser-based massively multiplayer online game (MMOG), allows large-scale complex behavior to emerge, and we draw parallels between virtual-world LSCs and real-world LSCs. The LSC-related behavior that we are interested in identifying deals with the conditions that lead a participant in the virtual environment to engage and actively participate in a LSC, with the goal of informing an agent-based model (ABMs) that predicts when any one participant is likely to engage in conflict. We identified virtual-world behavioral analogues to real-world behavior of interest (i.e., insurgent behavior), and link the virtual behavior to a (previously derived) theoretical framework that analyzes the determinants of participation in civil war. Within this research, we have applied known social theories to determine the factors that inhibit or drive participants to join an ongoing conflict.

From our analysis techniques, we will apply this research to known ABMs to determine the utility of virtual-world data as a means for validation of social behaviors. If successful, this research will provide greater insight into how to use this newfound resource to create more realistic simulations of sociological phenomena.

Quantitative Adaptation Analytics for Assessing Dynamic Systems of Systems 158767

Year 1 of 3

Principal Investigator: J. H. Gauthier

Project Purpose:

Our national security is built of dynamic systems of systems (dSoS) — the military, homeland security, the nuclear weapons complex, and organizations therein. These dSoS are collections of systems that interact and reconfigure over time in response to internal (e.g., costs) and external (e.g., threat environment) pressures. The problem is how to structure and manage a dSoS in an efficient and effective way, a way that maximizes multiple functional capabilities (with interdependencies) of a dSoS as missions and threats change and the collection of systems must be expanded or reconfigured. This problem is of concern to many, including the US Army as stated in TRADOC 525-7-7: “...the U.S. Army will require capabilities to plan and design, construct and deconstruct, and operate and manage base camps in the most effective and efficient manner. The lack of a holistic system of systems approach results in an enormous effort...without regard to the adaptability of design...consistently incorrectly sized and not adaptable...” Research on dSoS adaptability is lacking, but research in related areas has centered on qualitative behavior — self-organization, learning, and emergence. Our project is novel because of the concentration on quantification, on generality of the analytics, on national security dSoS, and on a new treatment of adaptation.

How to achieve more efficient and more effective national security dSoS, given budget pressures and constantly changing threat environments, is currently unknown. Our research focuses on the following topics: 1) quantitative adaptation metrics, 2) rules enabling successful adaptation, and 3) analytic tools that are useful and generally applicable to a variety of national security dSoS. This research will expand our knowledge of what constitutes effective dSoS adaptation in its many forms — flexibility, resilience, and robustness. Such dSoS adaptation is a technically challenging problem, and creation of a generally applicable capability to analyze dSoS is beyond the funding scope of national security organizations.

Ultra-Stable Oscillators for RF Systems 158768

Year 1 of 3

Principal Investigator: B. L. Tise

Project Purpose:

The purpose of the project is to utilize ultra-stable clocks to improve performance of radio-frequency (RF) systems and to develop new waveforms and new processing techniques to further reduce the size and power of RF receivers while increasing performance of these systems. This work stands to benefit a broad array of technologies relevant to numerous laboratory, DOE, and DoD missions.

Differential Emitter Geolocation 158769

Year 1 of 1

Principal Investigator: J. J. Mason

Project Purpose:

The geolocation of radio-frequency (RF) emitters is a crucial capability of overhead electronic systems that support a wide variety of national security needs such as personnel recovery and asset tracking. Often users of these systems desire more accuracy than the systems provide.

The purpose of the project was to determine if the differential-carrier-phase technique used in high-accuracy global positioning system (GPS) could be adapted to geolocate RF emitters. Some of the key differences in the emitter geolocation problem are:

1. GPS locates receivers whereas we need to locate transmitters.
2. GPS signals are indefinitely long, whereas we are interested primarily in emitter signals that are just a few seconds long.
3. Emitter location systems typically use fewer satellites than does GPS.
4. The needed emitter-location accuracy is generally a few meters whereas the GPS differential-phase technique can give errors as small as a few centimeters.

We did not discover any major issues connected with item 1, but an actual demonstration will be required to prove this. On the other hand, we found that items 2 and 3 limited the achievable accuracy. In fact, for signals durations of seconds rather than minutes, we found that the desired integer solution could not be found, but the float solution could provide a significantly better position estimate than obtainable from the time-of-arrival (TOA) data.

Summary of Accomplishments:

We provided a deeper analysis of the differential-carrier-phase technique than existed in the literature. This analysis enabled us to conclude that it was physically impossible to determine the integer wavelengths in the differential paths for signals as short as we hoped to use. However, we found that even when the exact integers could not be determined, a floating-point estimate of them (called the float solution by practitioners) provided a great improvement in accuracy. For example, for some parameter sets, an order-of-magnitude reduction in error can be achieved over the TOA solution.

Significance:

This work suggests a higher-accuracy tag-geolocation estimate is possible for some important national systems. The largest obstacle to using the proposed technique will likely be the requirement that a reference emitter is near to the emitter being located. Exactly how near the reference must be depends on system parameters, such as operating frequency, and needs further investigation.

Moving-Target Detection and Location in Terrain using Radar 158770

Year 1 of 3

Principal Investigator: D. L. Bickel

Project Purpose:

During the last decade, the requirement for detection of moving objects for intelligence, surveillance, and reconnaissance has grown dramatically. More recently, government agencies are incorporating various forms of motion-intelligence information into their purview to help support this growing demand. Radar sensors, including joint surveillance and target attack radar system (JSTARS), have proven to be invaluable for detecting moving objects in battlefield and intelligence, surveillance and reconnaissance (ISR) applications.

One of the currently unsolved problems in using radar systems for detecting moving objects is achieving satisfactory performance in complex environments that include steep terrain. For the radar system, the difficulty arises in the filtering of stationary clutter due to complications introduced by the terrain and radar geometry. The purpose of this project is to address this problem of detecting moving targets in steep terrain via a combination of new radar sensor modes and signal-processing algorithms.

Electronic Battle Damage Assessment (eBDA)

158773

Year 1 of 3

Principal Investigator: J. T. Williams

Project Purpose:

Tactically, one of the greatest impediments to the application of high-power microwave (HPM) weapons is the current inability to assess their effect on the intended target, battle damage assessment (BDA).

The problem is further complicated since the effects achieved by such weapons can be temporary or permanent and are sometimes not repeatable given minor changes in the engagement scenario. Hence, the BDA tools for nonkinetic weapons, and even kinetic weapons targeting electronic systems, should be based upon on-site intelligence and electronic sensing, as proposed here.

An effective, electronic BDA (eBDA) tool should be able to detect system changes based upon electromagnetic (EM) observables, assess the operational state of the target system given the detected system changes, and classify the success of the attack. Critical to developing such eBDA tools is the identification of tactically feasible EM observables that can be exploited by either active or passive electronic sensing systems. At close ranges, we have successfully identified many such observables in realistic environments. The intent of this project is to develop the techniques to measure state-related electromagnetic observables from relevant target systems at range. The outcome of this effort should be a TRL-5 prototype system that demonstrates effective eBDA principles and techniques.

Without a doubt, the proposed effort is extremely challenging and fundamental in nature. Many of the passive EM observables that can be used effectively for eBDA are low power level and clustered with other less-relevant emissions and background noise, making detection at-range very challenging. In addition, the design of active EM signals that can be used to interrogate a specific target and produce measurable responses that can be related to its state is a relatively unexplored discipline. However, many of these issues should be resolvable when proper measurement and signal-processing techniques are brought to bear.

Developing Deeply Integrated GPS/INS Navigation System for High-Dynamic Applications

158775

Year 1 of 2

Principal Investigator: J. D. Madsen

Project Purpose:

We propose utilizing Sandia's previously developed global positioning system (GPS) receiver, the high-dynamic tracking receiver (HTR), to explore methods for maintaining GPS carrier phase-lock in ultra-high dynamic environments in excess of 50G acceleration and 100G/second Jerk. Emerging missile programs of national interest require high precision navigation through ultra-high dynamic conditions. These programs include conventional prompt global strike (CPGS), boost-phase ballistic- missile defense intercept, and Automated Flight Safety Systems. High-precision navigation can be achieved through the use of GPS carrier-phase measurements. To leverage the carrier-phase measurements requires that the GPS receiver continuously track the GPS satellite carrier signal. A standalone GPS receiver can improve its tracking performance in dynamic conditions, but in doing so it sacrifices its ability to track in low signal or noise environments. This is an unacceptable tradeoff in the proposed application space. Upon conclusion of this project, the HTR will maintain carrier lock in ultra-high dynamics and in noisy conditions by the use of advanced track loop designs complemented by auxiliary aiding information from a tightly coupled inertial navigation system.

No commercially available off-the-shelf GPS receiver exists that tracks successfully in ultra-high dynamic environments. Given the perceived small market for high-precision navigation in these type environments, GPS receiver developers are hesitant to invest the necessary internal venture capital to realize these type receivers. Also, receiver developers typically lack the necessary experience in the ultra-high-dynamic domain to competently form signal-tracking requirements for these applications. Development of this capability by Sandia will fill a niche that is currently not being filled; and when successfully demonstrated, it will be a differentiating technology for Sandia that can be applied to a wide variety of hypersonic vehicle applications that require navigational precision.

Structural Kinetic-Energy Warhead for Scaled and Multi-Platform Applications 158776

Year 1 of 2

Principal Investigator: L. R. Payne

Project Purpose:

The concept of the kinetic energy penetrator (KEP) warhead is to use the kinetic energy of a high-velocity approach vehicle that explosively deploys thousands of penetrating rods to destroy a target. The explosives deploy rods in a pattern creating a potentially lethal footprint on the target. Past Sandia concepts utilizing KEPs involved significant packaging or parasitic mass that this study will eliminate to increase the mass available for rods. In an era when using nuclear weapons carries grave political risks, effective alternative conventional warheads are needed to address evolving adversarial threats to national security.

In a KEP warhead, dispersed, high-density tungsten rods impart kinetic-approach energy on targets. A large mechanical structure is required to support these high-density rods in dynamic delivery environments; this structure takes up weight and volume that could be better used for more rods and disrupts optimal rod deployment patterns. We propose to develop a compact KEP warhead that eliminates the need for support structure by mechanically bonding the tungsten rods together to create a self-supporting structure. Several concepts for bonding will be investigated including brazing rods together, sintered rod assemblies, and other state-of-the-art bonding techniques. The goal is to create a self-structural system that can maximize packaging efficiency, warhead scalability, and rod-deployment pattern predictability.

Our approach departs from traditional KEP warhead concepts; our approach is to use innovative material sciences and manufacturing processes to create a bonded rod system to support the warhead itself. Early phases will incorporate subscale testing and cost-effective surrogate materials. The major risk in this concept is whether sufficient structure can be obtained to withstand the mechanical environments of flight and of even more extreme sled-track tests while preserving the desired rod-distribution patterns. Additional risks include whether complex KEP systems can be computationally modeled with high enough fidelity to provide adequate design feedback.

Inferring Organizational Structure from Behavior 158780

Year 1 of 3

Principal Investigator: T. L. Bauer

Project Purpose:

Inferring the existence of programs conducted in secret under the guise of dual-use research requires inferring the existence of hidden networks of individuals and institutions from observable behavior. We will advance the state of the art in algorithms for detecting these networks by introducing the use of temporal correlations among behaviors, leveraging both information sources and metadata. We will validate the algorithms against two data sets. This will result in new algorithms and technology for applying them.

A lack of real-world data sets with both social network and behavioral information (as opposed to poll results, for example) has impeded the development of valid models for inferring social networks. However, newer data sets and recent research suggest that this problem might now be tractable. The rapid increase in crowd-sourced applications like Wikipedia is providing a rich set of data with both a record of behaviors and a set of direct interactions among individuals. Data sets with network ground truth are needed to develop and validate models, before applying them to national security settings where content and meta-data alone are available.

This research will advance the state of the art by focusing on temporal correlations in behavior.

The ability to discover organizational structure from observable behavior would address multiple national security problems, such as technology surprise and nonproliferation. However, it is itself a basic scientific question. The core capability for doing this is most appropriately developed and validated in the context of scientific investigation before being transitioned to specific use.

We will focus on using implicit evidence, such as two people editing the same page, editing documents in the same topic, or participating in the diffusion of data in similar points. While none of these examples show direct connections among people, they do show that the people are similar in certain ways and may also be connected.

Frequency Translation to Demonstrate a “Hybrid” Quantum Architecture 158782

Year 1 of 3

Principal Investigator: D. L. Stick

Project Purpose:

Modern encryption relies on the computational complexity of factoring large numbers with a classical computer. In 1994, Peter Shor developed a factoring algorithm for a quantum computer, one governed by quantum mechanics, which factors numbers more efficiently and threatens to compromise modern encryption. Most experimental work in quantum computing has focused on systems of identical quantum bits, or qubits. However, a large-scale quantum computer will likely be composed of several types of qubits, with each qubit selected to exploit its advantages for the overall system. Photons are a natural choice for coupling different qubits due to their ability to travel great distances quickly.

Due to energy structure differences, one qubit type cannot be directly coupled to another of a different type. Instead, one needs a quantum interface to convert the energy (frequency) without destroying the quantum information, which the photon is carrying. A solution to this interfacing problem is nonlinear optics (NLO) and quantum frequency conversion (QFC) of photons. We propose to demonstrate QFC with photons emitted from different ion qubits by making the photons emitted from one ytterbium ion, Yb^+ , indistinguishable from photons emitted by a calcium ion, Ca^+ . This will be the world's first photonic coupling of different types of qubits. If successful, this technology will enable new quantum architectures and distributed quantum computing.

This research will demonstrate a proof-of-principle experiment that may fundamentally change our current ideas in quantum information processing. This work demonstrates the coupling between the same types of qubits, trapped ions, but of different ion species which lays the foundation for coupling drastically different types of qubits, such as ions and quantum dots. This research aims to demonstrate the required building block for enabling quantum hybrid computing and architectures. This important, innovative technology will allow Sandia to demonstrate new classes of quantum-information-processing devices.

Cross-Domain Situational Awareness in Computing Networks 158783

Year 1 of 3

Principal Investigator: S. A. Mulder

Project Purpose:

There exists a large theoretical gap in our ability to understand the code executing on our computers and what, in practice, is actually understood. This may be illustrated by the fact that manual reverse engineering can, in practice, unravel almost all programs and characterize their functionality, given enough time. Automated defensive processes, however, rely on static signatures and very simplistic feature characterization to identify malicious software. In reality, context is critical to determining whether executable code should exist in a given system and whether its presence indicates malicious intent. In theory, we should have access to information about what capability is present on our information systems, including what code exists in storage (hard disk, flash), and what is executing in memory. Previous work in this area has provided us with rich feature extraction of both stored and executing programs. Two notably missing elements are closely related: scalable program understanding which leverages the analysis of millions of programs to characterize individual programs, and a cross-domain analysis that provides both host and network context. The purpose of this project is to create a system that allows us to perform experiments combining automated program understanding and context analysis.

Full program understanding is a fundamentally difficult problem as it builds on at least one problem (correct disassembly) for which it can be proven impossible to construct a single algorithm that always leads to a correct yes-or-no answer. The best that is generally achievable is a series of approximations of increasing semantic meaning and probability. Approaches that examine individual programs without context are limited to relatively simple heuristics. Combining high-speed analysis and characterization heuristics with a scalable architecture that allows us to leverage prior analysis of millions of files should allow us to gain a deeper insight into the structure of the functionality on the network than has ever been achieved.

Nonlinear Decision Theory Applied to Co-Hosting Analysis for National Security Space Payloads

158784

Year 1 of 3

Principal Investigator: S. M. Gentry

Project Purpose:

Due to the high expense of providing access for space payloads to high earth orbits (geosynchronous and medium earth orbits), national security space mission planners are encouraged to coordinate disparate payloads or missions on common host spacecraft. This practice of co-hosting potentially creates lower-cost opportunity for the mission(s) involved, but practically results in unforeseen technical and programmatically detrimental effects on the outcomes of the combined missions. How can mission planners anticipate these effects and follow a technically rigorous approach of identifying and blending space missions that ultimately achieves combined technical goals that may not have been possible independently?

This collaborative research between Sandia and the MIT Engineering Systems Division will leverage MIT's 'Family of Systems,' nonlinear objective function, and mixed discrete-continuous design vector approaches to develop a comprehensive framework for quantitative evaluation of co-hosting for national security missions and payloads. Utilizing lessons learned from the space based infrared system (SBIRS), the global positioning system (GPS), and the United States nuclear detonation detection system (USNDS) as examples both of past co-hosting decisions, and also candidates for future co-hosting decisions, this research will develop a framework for the decision theory supporting co-hosting assessments, with an associated emphasis on nonlinear decision analysis suited for educating these national-level technical trade studies.

Current experience in the space acquisitions community suggests that this problem is highly subjective and therefore solved principally via programmatic assessments. Decisions are not usually backed by a modern decision-theory approach that appropriately identifies critical technical and programmatic variables, but more importantly stakeholder value systems, and blends these factors via nonlinear objective functions and mixed discrete-continuous design vectors. If a decision-theory approach following this line of research can be applied to the SBIRS, GPS, and USNDS co-hosting problem successfully, it is expected that the same approach, tools, and lessons learned may be transferable to other national security space-mission analyses for co-hosting.

Learning from Nature: Biomimetic Polarimetry for Imaging in Obscuring Environments

158785

Year 1 of 3

Principal Investigator: S. A. Kemme

Project Purpose:

Imaging in obscuring surroundings, such as fog, smoke, dust, and under water, occurs in one of the most difficult imaging environments encountered on earth. However, many key national security interests rely on communicating and seeing in these obscuring environments, such as helicopters landing blind due to obscuring dust or communicating/imaging through clouds and water. Even modest extensions in imaging ranges in these extreme turbid environments would be a technological breakthrough and have wide-ranging impact on turbid-media signaling, imaging, and communications. This project, in collaboration with the University of Arizona, seeks to develop passive optimal-polarization vision, utilizing both linear and circular polarization signatures, which has been shown to increase imaging distances three times compared to standard intensity imaging. Because the environmental variables (e.g., imaging wavelength, particle-size density, size distribution, and index of refraction) are so diverse, specific optimization for imaging in critical conditions have not been performed. We will systematically develop polarimetry-imaging schemes specifically tailored for obscuring environments crucial to national-security applications (clouds, dust, oil plumes) through a combination of simulation and experimental techniques. This will allow the exploitation of polarimetry for tagging, tracking, and locating applications and for improving imaging in turbid media that is of interest for a broad application set including environmental monitoring, underwater communications, and rocket-plume detection.

The stomatopod crustacean (mantis shrimp) has evolved an exquisite vision platform and has the capability to see in full polarization. Biologically evolved systems are often supremely adapted to their environment, solving complex problems that maximize visual information while minimizing metabolic energy consumption and signal-processing requirements. These biologically evolved systems should be the inspiration for future imaging systems. Findings can be extended to both terrestrial and space-based environmental imaging systems where turbidity is introduced by pollution, smoke, and clouds.

Parallel Object-Oriented Programming of FPGAs and CPUs 158786

Year 1 of 1

Principal Investigator: J. A. Brooks

Project Purpose:

As lower power consumption and longer battery lives become a key element of the mobile computing domain, people are looking towards field-programmable gate arrays (FPGAs), application-specific integrated circuits (ASICs), and other embedded solutions to achieve lower power requirements. Traditional CPUs provide ease of programmability but consume significant power. FPGAs offer incredibly low power consumption when compared to CPUs; an FPGA consumes on average 1% of the power of a traditional CPU. Tools to program FPGAs are often counter-intuitive to the lay programmer as many of the concepts involved in software and hardware programming are different. The goal of this project is to have a single programming system to control multiple CPUs and FPGAs, where objects in-memory on the CPU can reference an object stored on the FPGA. Such a design will allow a blurred distinction between the CPU and FPGA and make available for many users the ability to program complex, concurrent, distributed CPU-FPGA hybrid systems, meeting requirements of both low energy consumption and competent performance.

The increase in popularity of portable and mobile devices has not been accompanied by an equal improvement in programmability of the low-level embedded hardware technologies. The demand is there for the ability to write understandable hardware code using language constructs that are easily understood to achieve products with the lowest possible power consumption. Despite the potential, little work has been done in this field and, therefore, highlights a risk. Since there is little existing research in this area, significant obstacles may be encountered. One example is that the traditionally accepted methods of implementing abstract language constructs may be inefficient, or even incompatible, with the way that FPGAs structure a program. Inherent in our proposal is not only the work to create these abstractions for programming an FPGA, but the process of discovery regarding what works well and what does not. The work is in collaboration with UCLA.

Summary of Accomplishments:

We created a compiler which enables a full tool chain that leads from high-level object-oriented Virgil code to low-level VHSIC hardware description language (VHDL) designs, allowing software engineers to easily reap the enormous energy consumption benefits that FPGAs have to offer while still exhibiting reasonable performance.

The experimental benchmarks demonstrated that some types of object-oriented code can be made to run more than twice as fast while using 1/8th the energy if compiled and executed on an FPGA versus a low-power Intel Atom processor. We also learned that not all algorithms run faster when migrated to the FPGA, though all our benchmarks show a significant power savings. Using our compiler to move the algorithm to an FPGA can be an excellent deployment method when low power consumption is more important than performance.

Significance:

Low-power processing capabilities are an important enabling technology on remote-sensing platforms where power and cooling can be driving design factors. Allowing programmers to write in high-level object-oriented languages makes the development process efficient while still reaping the benefits of an extremely low-power implementation. Future mobile computing systems will demand more performance using fewer resources, and FPGA implementations are one way to achieve those goals.

Enhanced Methods for the Compression of SAR Video Products 159304

Year 1 of 2

Principal Investigator: J. G. Chow

Project Purpose:

Conventional video compression methods are block-based, which introduces visually disturbing artifacts into the compressed data. The goal of the proposed work is to investigate improved methods for the lossy compression of video synthetic-aperture-radar (SAR) magnitude data and SAR products such as coherent change detection (CCD) and normalized CCD products (NCP). These methods will create a pre-processing algorithm intended for SAR products with the goal of retaining fidelity on key features of intelligence interest in the imagery under high compression ratios and over variable terrain types, such as desert, foliage, urban, and maritime. We plan to investigate advanced compression approaches for three-dimensional video SAR data sets, with the goals of demonstrating a proof of concept.

Nitrous Oxide-Hypergol Propellants 161633

Year 1 of 1

Principal Investigator: M. C. Grubelich

Project Purpose:

Nitrous oxide-hypergol (NOH) systems have been investigated very little over the years, yet there is little scientific reason why an NOH system could not be developed. A bipropellant for use in an extraterrestrial (e.g., satellite) microthruster would have advantages over current technology in that current fuel-oxidizer propellant systems require an ignition system. Ignition in zero atmosphere conditions is problematic from a physics standpoint and also requires on-board electronics. These electronics increase the payload and also increase the statistical chances of total system failure. An oxidizer-hypergol bipropellant does not need an ignition system. It is initiated by enabling contact of the two species (a valve) and can also be turned on and off as needed. Advantages of NOH versus other systems are that nitrous oxide is environmentally benign and cost-effective. Nitrous oxide and known hypergols (triethylaluminum, triethylborane, silanes, either neat or in a solvent such as an alcohol) may provide a very efficient replacement for hydrazine (non-bipropellant)- based fuel systems. The work is in collaboration with New Mexico Tech.

Optimal Adaptive Control Strategies for Hypersonic Vehicle Applications 161863

Year 1 of 3

Principal Investigator: J. M. Parish

Project Purpose:

The purpose of the project is to develop a reliable model-based control strategy for agile flight vehicles subject to large uncertainties and undesirable multi-body dynamic behaviors. Unlike traditional control approaches, model-based nonlinear control methods are particularly well suited to construct tractable control designs for highly maneuverable vehicles subject to large aerodynamic uncertainties. In this method, nonlinear vehicle dynamics are assumed to be largely “cancelled out” in an inner control loop. However, the unexpected presence of unmodeled dynamics has been shown to cause controllability issues, instabilities, and failures in both simulation and flight of actual vehicles. In general, this undesired behavior results from neglecting key nonlinearities in the rigid-body vehicle model typically employed in nonlinear control. Some integration of elastic effects into the control approach has been considered for similar types of vehicles, but neither multi-body nor elastic effects have been investigated for this class of vehicle. Thus, control of these more comprehensive vehicle dynamical models remains a challenging, outstanding problem. The proposed work will develop a control strategy for a multi-body dynamic model of a vehicle with consideration of low-frequency body elastic modes. This hybrid approach of simultaneously investigating control of both multi-body and structural dynamics is novel for control design for this class of vehicles. This broader view synthesizes existing control methods to enhance the capabilities of advanced vehicle concepts. Furthermore, these developments will help guide development of future vehicle concepts by providing a more holistic modeling and control approach for assessing performance of candidate flight vehicle designs.

Athermal Spectro-Polarimetric Enhancement (ASPEN) 164670

Year 1 of 2

Principal Investigator: J. C. Jones

Project Purpose:

Polarization is a fundamental optical phenomenon that provides a measurement of surface roughness, shape, and structure, but it has yet to be fully exploited for remote sensing applications. Channeled spectropolarimetry (CS) is a hyperspectral polarization measurement technique that requires no moving parts, making it ideal for implementation on moving platforms. Developed extensively over the past decade, CS instruments have been demonstrated in the visible and infrared, both in the laboratory and with fielded instruments.

The most challenging aspect of the CS technique is maintaining system calibration. The most robust calibration procedure developed to date involves acquiring a reference polarization measurement, which is used to characterize the CS system. However, due to the effects of thermal fluctuations on CS elements, this referenced-based calibration can often introduce significant errors in the resulting data products if there is a change in the environment between the acquisition of the reference data and of the data for the unknown target of interest. The simplest workaround for dealing with this calibration drift is to recalibrate the system frequently, often directly before or after every test measurement. This solution can be problematic for field deployments, especially under conditions of rapidly changing environmental conditions, unknown target frequency or location, etc. Due to these calibration-related performance limitations, the potential of CS systems has yet to be fully realized.

This work will focus on demonstrating and testing a new type of CS system that will leverage an athermal crystal technology developed for another application to significantly reduce the thermal calibration errors that can be problematic with CS systems. The ultimate outcome of project success is anticipated to be a proof-of-concept demonstration of a thermally insensitive CS (TICS) benchtop system that requires minimal recalibration and a preliminary design for a TICS prototype that would be deployable aboard remote vehicles.

Investigating Dynamic Hardware- and Software-Checking Techniques to Enhance Trusted Computing

164671

Year 1 of 3

Principal Investigator: C. Jenkins

Project Purpose:

The purpose of this project is to develop and demonstrate a new approach to designing secure computing systems. Currently, the computer world is flooded with spam, viruses, malware, and other source of misbehaving programs. Current solutions tend to fix one problem area and shift the attackers to another area. For example, the Never eXecute (NX) bit helped solve stack and buffer overflow problems. The outcome was new attacks utilizing return-oriented programming and heap-execution attacks. This project will review and inspect the way we design computer systems.

Traditionally, all security and program isolation was done by the operating system (OS). Over time, even the OS has been attacked and become vulnerable. This work looks at defining different domains for various parts of a computer system: functional, enforcement, reporting, and security. Trusted execution platforms such as ARM Trustzone® has potential for such a design. The goal of the project is to leverage existing software principles and designs and couple them with dynamic hardware- and software-checking techniques. This should allow for more robust and secure computer systems. Furthermore, this design should allow for substantial reuse of existing software, which will benefit cost and feasibility for deployment.

Mission-Capability-Analysis Environment for End-to-End Performance Assessment of Space Systems

164892

Year 1 of 3

Principal Investigator: D. P. Woodbury

Project Purpose:

By leveraging its strengths in remote-sensing-component technologies, Sandia has developed analysis capabilities to support high-fidelity empirically based simulations and yield verified accurate end-to-end sensor performance estimates of electro-optical infrared (EOIR) systems. Current analysis capabilities, however, are limited only to designed and tested remote-sensing assets. Furthermore, this simulation code provides mission-optimization tools only for specific systems based on experimentally determined parameters, which are unknown for envisioned EOIR designs. The combination of required mature sensor-characterization inputs and a lack of parameter-optimization capabilities for a variety of systems prevent utilization of the existing code for rapid mission-capability performance assessments of future EOIR systems. The goal of this research is to develop a target-based design and analysis environment that bridges the gap between literal mission needs and payload design requirements, without which there is a risk of making incorrect investing decisions in future space-based EOIR systems and technologies.

The key innovations of the proposed analysis environment are: 1) identifying the multidisciplinary set of first-principal physical constraints which couple the mission-critical design parameters of EOIR space systems and 2) exposing this high-dimensional, non-linear, mixed-discrete-and-continuous design space for improved parameter-selection capabilities to support mission requirements. First-order EOIR system requirements can be based on a finite number of fundamental physical parameters, which provide the backbone of a system's performance characterization. This multidisciplinary set of variables can be partitioned into three sets of parameters which describe the desired mission scenario, the external conditions imposed on that scenario, and the payload design itself. Along with identifying these base sets of critical design parameters, we must also ascertain the physical constraints between these parameters and how parameter uncertainty evolves through these applied constraints. Finally, the performance of the system must be related to specific mission scenarios and detectability metrics must be identified in terms of quantifiable measures of mission success.

ENERGY, CLIMATE, AND INFRASTRUCTURE SECURITY INVESTMENT AREA

Projects in this investment area focus in one of three objectives, namely: to accelerate the development of transformative energy solutions that will enhance the nation's security and economic prosperity, to understand and prepare the nation for the national security implications of climate change, and to develop and apply analytical approaches to secure the nation's critical energy infrastructure against natural or malicious disruption.

Tier 2 Development of Sandia's Air Bearing Heat Exchanger Technology Project 151304

This project has developed a conceptually unique heat exchange technology, the *Sandia Cooler*. This approach entailed solving three problems that limited the rate at which traditional fan-driven exchangers could move heat away from the source of a heat-generating device (such as a computer microcircuit board) to the external environment. First, a boundary layer of “dead” (motionless) air enveloping all surfaces of extant heat exchangers created a bottleneck. Instead of an active forcing of heat away from the heat source, some heat transfer occurred passively via diffusion—rather slowly. Supervening this bottleneck was a major challenge because it sets a limit on the efficiency of an air-cooler. Second, as heat-exchanger fans move heat, they inevitably become fouled by particulates and other contaminants in the air. And third is the issue of fan noise as the fans necessary to exchange heat increase in size and rate of rotation.

The solution to these challenges is the ingenious finned heat exchanger developed in this project. It rotates at about 5000 rpm upon a thin (0.001-inch) layer of air above a base-plate in contact with the device to be cooled (a computer CPU, for example); this means that the bearing for the cooler is air, rather than some mechanical structure, hence its name, “Air Bearing Heat Exchanger.” The rapid rotation of this finned “impeller” pumps air centrifugally from that thin layer, transferring heat to the structure's fins, which then dissipate that heat to the external surroundings. This rapid rotation and its pumping effect eliminates 90% of the dead air bottleneck. The high-speed rotation virtually eliminates particulate fouling of the fins, and their highly aerodynamic structure significantly. In this phase 2 project, the issue is the physics necessary to scale the technology up to larger heat-exchange situations, to a TRL-level-4-to-5 technology appropriate for energy sector applications.

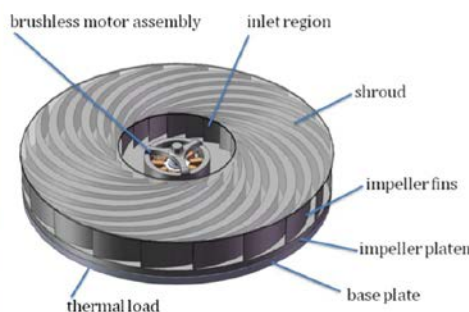
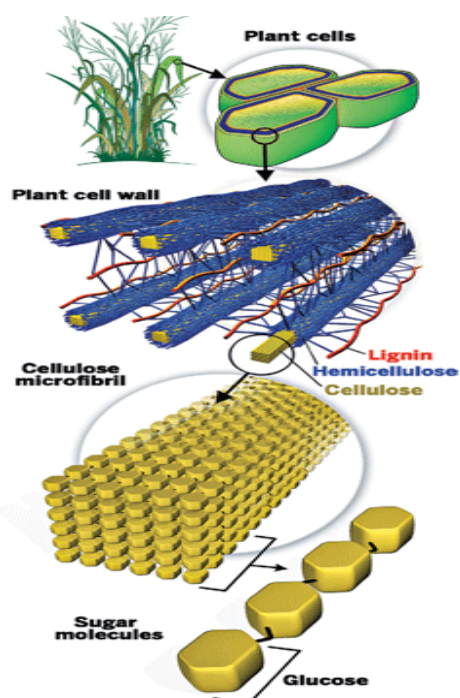


Photo (left) and diagram (right) of the heat impeller

Guiding Options for Optimal Biofuels Project 148066

This project is researching a detailed overview of the processes, interrelationships and feedbacks by which biofuels are produced from plant biomass, and then distributed to consumers, who utilize it in fueling their transportation needs. The project-developed model looks beyond existing technologies and infrastructure in order to probe the fundamental constraints and trade-offs affecting the deployment of such biomass-derived transportation fuels, integrating across temporal, spatial, and conceptual scales in a multidisciplinary fashion that informs better decision making given uncertain data inputs. The project's simplified models representing conversion of biomass to liquid transportation fuels are incorporated into a broader multiscale and multidomain model framework that couples the selection and development of feedstocks and conversion processes to provide a basis for exploring the entire pathway from agricultural inputs to the end use of the fuel.



Schematic representation of the early stages of biofuels production encompassed by this model: extraction of cellulose from plant cell walls and its hydrolysis to glucose (which is then fermented to ethanol and other biofuels).

Energy, Climate, and Infrastructure Security Investment Area

Advanced Battery Materials for Improved Mobile Power Safety 141614

Year 3 of 3

Principal Investigator: C. Orendorff

Project Purpose:

The most significant limitations in lithium-ion battery technology for transportation power/vehicle electrification are safety and reliability issues. While remarkable improvements have been made to anode and cathode materials safety, the most common field failures of electrolyte and separator represent notable hazards and have largely been overlooked until recently. In addition, the drive toward higher energy and power densities in hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs) will continue to push the limits of conventional separator and electrolyte stability. It is critical to understand that safety and reliability issues are inherent in all systems, independent of the push toward high energy or power HEV and PHEV cells and may preclude any of these emerging technologies and materials from being widely adopted. The objective of this work is to better understand degradation of battery electrolytes and separators and to mitigate the hazards associated with these processes through materials processing development, full-cell performance evaluation and abuse testing. This project has fundamental and applied components that complement programmatic testing and evaluation objectives. There are important technical challenges to consider in this project that include: 1) studying the electrochemical and thermal stability of sulfonamide/hydrofluoroether (HFE) electrolyte systems, 2) determining the mechanisms of gas formation and degradation of battery electrolyte, 3) separator material processing and scalability, and 4) cell-level evaluation and abuse tolerance of cells with these components. Sandia is recognized as a world leader in safety and reliability evaluation of energy storage systems, specifically lithium-ion cells for transportation power. Our detailed understanding of the issues related to battery safety/abuse response makes us uniquely qualified to pursue the development of mitigation strategies and to partner with others in these efforts. When successful, this project will incorporate all of these aspects of fundamental understanding, evaluation, and mitigation that will expand Sandia's capabilities.

Summary of Accomplishments:

Several noteworthy achievements were made on the electrolyte aspect of this project. Performance trade-offs were determined for HFE-based electrolytes in full lithium-ion cells as compared with conventional electrolyte systems in this battery type. This provided a baseline for understanding the viability of these electrolytes in the market for lithium-ion. Nonflammable behavior of HFE-based electrolytes was also determined under test conditions that are meaningful to cell failure modes. Together with this testing is the development of test methods for determining electrolyte flammability under actual cell failure modes. This accomplishment is particularly important, given that much of the nonflammable electrolyte development in this research community frequently lacks adequate testing and characterization. This work has addressed this issue of continuity between the development and testing efforts to better evaluate these materials in cells. Tools to make autoignition temperature measurements under ambient pressure relevant to battery systems were also developed to better understand the fundamental ignition properties of these electrolyte solvents.

Accomplishments were made in the area of separator development, as well. The development of poly(ester) separators has shown that improved separator thermal stability can be achieved without sacrificing performance (even at the developmental scale). Higher temperature stable separators can also be made using unique manufacturing processes that can be cost competitive and applied to existing battery fabrication technologies.

Significance:

The accomplishments of this project will contribute to Sandia and DOE missions in transportation energy, energy security, and electrochemical energy storage (HUB activities, etc.). This project will also have an even greater impact on the broader S&T community. For example, the electrolyte flammability testing that has been developed as part of this work could potentially be adopted by a number of test manuals (SAE J2464, UL, USABC, etc.) en route to becoming a certified test procedure that would influence how future batteries are evaluated.

Refereed Communications:

C.J. Orendorff, T.N. Lambert, C.A. Chavez, M. Bencomo, and K.R. Fenton, “Polyester Separators for Lithium-Ion Cells: Improving Thermal Stability and Abuse Tolerance,” to be published in *Advanced Energy Materials*.

Bridging the Gap between Atomistic Phenomena and Continuum Behavior in Electrochemical Energy Storage Processes

141615

Year 3 of 3

Principal Investigator: J. A. Templeton

Project Purpose:

One of the most significant impediments to advances in electrochemical energy storage lies in the gap between fundamental understanding of atomistic phenomena and the understanding of the impact of these phenomena on system performance at device scales. Atomistic models (density functional theory [DFT], molecular dynamics [MD], and Monte Carlo [MC]) provide insight into such phenomena and a computational means to quantify these, but such models are too computationally intensive to address device-scale behavior. Similarly, device-scale insight for design and optimization can be obtained through continuum models that are sufficiently fast, but these models account for only the simplest atomistic phenomena. There is thus a large gap between our ability to develop fundamental understanding and our ability to use this understanding to make rapid advances in energy storage technologies. The goal of this project is to help bridge this gap through an innovative synthesis of atomistic and continuum approaches in which atomistic phenomena are captured through fast reduced-order integral methods that can be embedded directly into continuum-like models describing device-scale behavior. Such a synthesis requires very significant advances in three principle areas, forming the basis of our three project goals: 1) to develop fast but rigorous integral methods describing the electric double-layer structure, 2) to incorporate this description of the double-layer structure into integral models of viscous, diffusive, and electrophoretic transport processes, and 3) to develop accurate reduced-order integral descriptions of surface electrochemical reactions that explicitly account for both the double-layer structure and ion transport. Success in these goals will represent a major advance in our ability to incorporate atomistic electrochemical phenomena into device-scale simulations, thereby enabling accelerated innovation in materials and devices for electrochemical energy storage.

Summary of Accomplishments:

We utilized and developed new models in three main areas. First, quantum DFT calculations were performed, which discovered unanticipated water-ion complexes in confined spaces. This demonstrates the need for further investigations to understand the chemical structure in the Stern layer and incorporate it into lower-cost double layer models. Second, we developed a classical DFT model of the double-layer and validated it against MD simulations. Both atomistically informed models showed significant and consistent deviation from classical theory, while the DFT simulations were orders of magnitude less expensive than the MD. We also developed a simple polar solvent DFT model and have shown it to be in rough agreement with an MD water model, again at a small fraction of the cost. In the third area, we developed new methodologies to inform continuum transport models from MD simulations. We developed and implemented a new Green-Kubo formulation capable of estimating transport coefficients in-homogeneously, e.g., in the wall-normal direction of the electric double layer. We used this method to discover the magnitude and length scales of viscosity and conductivity in a double layer. In addition, we created a polynomial chaos expansion (PCE) of thermal conductivity and inferred the PCE coefficients using Bayesian inference applied to small MD simulations. We then demonstrated that the results could be used in a continuous Fourier model of heat transport. Finally, we developed a non-parametric representation to model non-Fourier behavior that often occurs in nanosystems.

Significance:

Consistent with the project's objectives, this work has provided a model of the electric double layer using DFT, which retains accuracy consistent with MD but requires orders of magnitude fewer computational resources. This model can be used to impact scientific discovery and particularly engineering analysis by providing a way to rapidly screen different device configurations. It is also efficient enough to be used in engineering codes for systems analysis. Similarly, techniques to extract transport coefficients mean cheaper continuum models can be used to efficiently understand nanoscale conduction and flows. Finally, we have quantified differences from existing theories in double layers.

Refereed Communications:

M.A. Saeed, A. Pramanik, B.M. Wong, S.A. Haque, D.R. Powell, D.K. Chand, and A. Hossain, "Self-Assembly of Ordered Water Tetramers in an Encapsulated $[\text{Br}(\text{H}_2\text{O})_{12}](-)$ Complex," *Chemical Communications*, vol. 48, pp. 8631-8633, April 2012.

J.W. Lee, R.H. Nilson, J.A. Templeton, S.K. Griffiths, A. Kung, and B.M. Wong, "Comparison of Molecular Dynamics with Classical Density Functional and Poisson–Boltzmann Theories of the Electric Double Layer in Nanochannels," *Journal of Chemical Theory and Computation*, vol. 8, pp. 2012-2022, May 2012.

First-Principles Flocculation as the Key to Low Energy Algal Biofuels Processing 141617

Year 3 of 3

Principal Investigator: J. C. Hewson

Project Purpose:

Algal biofuels can substantially contribute to energy diversity if certain barriers can be overcome. A significant hurdle is the energy/cost associated with harvesting and dewatering algae. In theory, algae flocculation could drastically lower harvesting costs, but flocculating mechanisms that are reliable, effective, and efficient have yet to be identified. The propensity of algae to flocculate can be related to the properties of the algal surface and its interaction with the water around it. Of key importance is the tendency of algal surfaces to develop a negative charge and the ability of ions in the water to alter the resulting electric double layer. We are pursuing a fundamentally scientific approach to understanding the algal-water interface and its dependence on water chemistry and algal life cycle. The objective is to identify conditions favorable to flocculation that take advantage of algal pool chemistry (salinity, pH, etc.), low-tech flocculating agents (clays, bubbles, etc.) and the influence of fluid dynamics on the floc evolution. The project is employing an iterative sequence of theoretical predictions leading to hypotheses to be tested experimentally to develop a comprehensive understanding of the algae-water interface physics at the scale of the electric double layer formed on the algal surface and at the scale of inter-algal forces. The interrelation between fluid flow and sticking affinity in evolving floc dynamics is also being studied with combined experimental measurements and predictive modeling that draws upon and reinforces the understanding developed at the scale of the algae surface. A combination of highly controlled experimental environments and those more typically experienced in scaled-up production systems are being studied to identify scaling challenges. The objective is a map of the flocculation potential as a function of water chemistry and low-cost additives and a predictive model of flocculation dynamics, given that flocculation potential could be applied to the future planning of algal resource development.

Summary of Accomplishments:

Results can be split into two broad areas. First, we measured and predicted algae and precipitate surface properties as functions of the water chemistry and algal lifecycle. Noteworthy new results have come in the understanding of the life cycle and culture conditions on the surface properties and in the prediction of properties for precipitates forming from bulk salts like calcium and magnesium. For example, concentration of chemical species (functional groups) on the algae surface varies over the changing stages of the life cycle leading to a change in the surface charge and a similar change in the quantity of flocculant required. The significance of the result is that for a growth strategy that includes increasing the algal oil content, harvesting is likely to become easier. We developed models that predict the surface chemistry for precipitates that form from these bulk salts. The bulk salt precipitates that we investigated included $\text{Mg}(\text{OH})_2$ (brucite), a calcium phosphate (hydroxyapatite) and CaCO_3 (calcite). The surface of these precipitates interacts with the algae surface during harvesting/flocculation. The models predict the surface state as a function the water chemistry (pH and salts present) allowing us to predict the affinity between these precipitates and the algae surface.

Second, we measured and predicted the change in the floc structure as a function of the shear energy. Measurements show that this is a factor in the degree of water removal. We carried out high-fidelity particle dynamics simulations that show for the first time the details of the floc restructuring process. These results are fed into macroscale models, and will ultimately be useful for optimizing the mixing energy put into flocculation processes.

Third, we measured the phase space over which algae can be effectively separated from the growth media in terms of the water chemistry, added flocculants, algae concentration, algae lifecycle and degree of mixing. Further, we related the boundaries of this effective separation phase space to more fundamental processes: some boundaries were linked to the algae and precipitate surface chemistry and the tools developed for those purposes predict those boundaries. Other boundaries are related to alga-alga interaction frequencies, and we developed population dynamics models, supplemented with floc structure information from this work, to predict these boundaries. In this way, we have enabled the prediction of the effective flocculation phase space.

Significance:

In the course of this project we have developed tools that will enable greater efficiency and reliability in the separation of algae from its growth media. This is an important step in assisting DOE Basic Energy Sciences in enabling algal biomass as an energy resource, reducing our dependence on petroleum and other forms of energy. While the project was specifically oriented toward algae separation, the majority of the tools developed are useful for separation processes in general.

Refereed Communications:

X. Zhang, P. Amendola, J.C. Hewson, M. Sommerfeld, and Q. Hu, "Influence of Growth Phase on Harvesting of *Chlorella Zofingiensis* by Dissolved Air Flotation," *Bioresource Technology*, vol. 116, pp. 477-484, 2012.

Novel Room Temperature Synthesis of Nuclear Fuel Nanoparticles by Gamma-Irradiation

141618

Year 3 of 3

Principal Investigator: T. M. Nenoff

Project Purpose:

Our primary project focus is the synthesis and characterization of surrogate-fuels nanoparticles (NPs) and their formation to bulk fuels. We are studying nanoparticle formation (through the room temperature chemistry of radiolysis and its effect on metal(s) solutions), composition (through use of proper surrogates, including depleted uranium (dU) and lanthanides (Y, Eu, and La) for americium), solution pH, and stability (nanoparticle surface protection) of the surrogate fuels. This research uses gamma-irradiation for the radiolysis of solvating water to perform room temperature synthesis of metal alloy and oxide NPs. The radiolysis will be performed at the Sandia Gamma Irradiation Facility (GIF) ^{60}Co source and in a newly built in situ microfluidics transmission electron microscope (TEM). Metallic and oxide alloys of varying compositions can be produced.

Production of bulk fuels from nanoparticles is of equal importance to this project. Both metal and oxide NPs have been sintered at Sandia California by in situ high temperature TEM; our UO_2 NP sintering experiments show sintering temperatures reduced more than 700 °C from bulk. In situ microfluidics TEM allowed for room temperature (RT) lanthanide-surrogate NPs growth in real time. Complementary modeling is key to the project. We used ab initio molecular dynamics (AIMD) to calculate the redox potentials of uranium species in water, and successfully developed and implemented mesoscale algorithms to simulate microstructural evolution during differential sintering.

The high creativity and innovation of this program are observed in both synthetic methods and goals: 1) low temperature synthesis and sintering conditions mean no volatility of fuel components, 2) high reproducibility of the products as pure/homogenous phases, and 3) an inexpensive method to make research quantities of fuel surrogates for science-based approaches DOE's (Nuclear Energy-Fuel Cycle Research and Development [NE-FCRD]) needs. We plan to leverage successes from this basic research, proof-of-concept program to basic research DOE's Office of Science, and/or applied-research DOE/NE fuels programs.

Summary of Accomplishments:

We accomplished our milestones for FY 2012. We successfully synthesized dU metal and dUO_2 nanoparticles, and characterized them by UV-Vis, TEM, high-resolution TEM/energy-dispersive x-ray spectroscopy (EDS). We also successfully synthesized RT lanthanide NPs (not easily detected in GIF experiments) using a newly designed and built in-situ microfluidics TEM. All reactions are salt-type (chloride/nitrate) and pH dependent.

We studied dUO_2 nanoparticles formation by radiolysis. The NPs (5 nm) were formed with maximum yield in aqueous reactions of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and isopropanol, pH=4, 5.5 rad/s, 10 days. Sintering temperature was determined to be 600 °C, a 700-1000 °C reduction in temperature than bulk.

We were successful in synthesizing pure dU NP formations. Aqueous solutions of UCl_4 and PVA organic in pH=1 yields maximum crystalline NPs (<3 nm). HRTEM and EDS indicate crystalline U (gamma phase) can be formed. With time (7days, in air) NPs transform to UO_2 . Surface modification, organic concentration polyvinyl alcohol (PVA) studies indicate induced stability of U NPs. Difficulty

with small NP sizes of alloys of U-La (e.g., La, Eu, Y) led to successful studies with the in situ microfluidics TEM.

We applied ab initio molecular dynamics simulations to U(III) and U(IV) in aqueous solutions. Using the PBE functional with DFT+U (U= 2 and 4 eV) augmentation of U 5f orbitals, U(III) has 8 waters in the first shell and U(IV) has between 7 and 8. AIMD calculations show the number of water molecules coordinated to U(IV) is the driving force that governs deprotonation events, and show that the physical pathway connecting U(III) to U(IV) involves the elimination of a proton from the uranium first hydration shell.

We have developed algorithms to simulate microstructural evolution during differential sintering under applied stress; our work shows that particle rotation has been eliminated as a sintering mechanism.

Significance:

This project addresses the areas of nuclear fuels and intrinsic and global security. In particular, it focuses on developing novel nuclear fuel systems via new fuel alloy/oxide phases for DOE/NE-Fuels Campaign needs. It also addresses intrinsic and global security by developing a method of introducing tags in fuel alloys for use in verification and safeguard systems (transparency and safe expansion of nuclear energy).

Refereed Communications:

T.M. Nenoff, B.W. Jacobs, D.B. Robinson, P.P. Provencio, J.-Y. Huang, S. Ferreira, and D.J. Hanson, "Synthesis and Low Temperature In Situ Sintering of Uranium Oxide Nanoparticles," *Chemistry of Materials*, vol. 23, pp. 5185-5190, November 2011.

C.G. Cardona, V. Tikare, B.R. Patterson, and E. Olefsky, "On Sintering Stress in Complex Powder Compacts," *Journal of the American Ceramic Society*, vol. 95, pp. 2372-2382, August 2012.

K. Leung and T.M. Nenoff, "Hydration Structures of U(III) and U(IV) Ions from ab initio Molecular Dynamics Simulations," *Journal of Chemical Physics*, vol. 137, p. 074502, August 2012.

Programmable Nanomaterials for Reversible CO₂ Sequestration 141619

Year 3 of 3

Principal Investigator: P. V. Brady

Project Purpose:

The purpose of this project is to adapt nature's primary CO₂ capture processes into an artificial setting. The DOE has set targets for cheaply and reversibly removing one billion metric tons of CO₂ per year to mitigate the contribution to global warming associated with the burning of fossil fuels. In nature, much of the CO₂ that we are introducing into the atmosphere is already being removed via: 1) partitioning of CO₂ into water (i.e., the oceans), and 2) biological processes. This project is exploring duplicating some of nature's reversible CO₂ capture processes by: 1) utilizing water as the capture agent, 2) utilizing enzymes such as carbonic anhydrase to promote the capture and release of CO₂ from water via the reversible conversion of relatively insoluble CO₂ gas into highly soluble carbonate ions, and 3) utilizing programmable polymers to reversibly switch the solution pH to mediate CO₂ solubility and/or enzyme activity. Project components include the following: 1) Programmable pH Buffers — acid-base groups that function as pH buffers have been incorporated into polymers that can be programmed with small temperature changes to promote reversible CO₂ \longleftrightarrow carbonate conversions, 2) Programmable Enzymes — experiments are being conducted on both native and engineered versions of the enzyme carbonic anhydrase in potential CO₂ processing environments, 3) Process Development — a small bench-scale system has been assembled and utilized for conducting CO₂ loading and unloading experiments. A larger modular system has been designed and will be tested to evaluate a range of potential CO₂ loading and unloading processes involving programmable polymers and enzymes, and 4) Theory and Modeling — modeling efforts are being conducted to evaluate loading and unloading mechanisms to provide design rules for improving both enzyme and polymer performance.

Summary of Accomplishments:

1. We developed a molecular understanding of CO₂ hydration and carbonic anhydrase activity.
2. We established a proof-of-principle experiment that performed the thermal cycles with and without the carbonic anhydrase and measured CO₂ uptake.
3. We developed new polymers that had a higher pH swing.

Significance:

Our efforts addressed the DOE initiative of scientific discovery and understanding by advancing the frontiers of science and engineering and, respectively, working out the molecular basis for carbonic anhydrase activity. We also demonstrated that a combined programmable polymer + enzyme system could capture CO₂. Additionally, this project's results contribute to knowledge required for CO₂ sequestration and climate change mitigation.

Refereed Communications:

D.M. Rogers, D. Jiao, L.R. Pratt, and S.B. Rempe, "Structural Models and Molecular Thermodynamics of Hydration of Ions and Small Molecules," *Annual Reports in Computational Chemistry*, vol. 8, pp. 71-127, 2012.

D. Jiao and S.B. Rempe, "Combined Density Functional Theory (DFT) and Continuum Calculations of pKa in Carbonic Anhydrase," *Biochemistry*, vol. 51, pp. 5979-5989, July 2012.

J.C. Kelly, M. Pepin, D.L. Huber, B.C. Bunker, and M.E. Roberts, “Reversible Control of Electrochemical Properties Using Thermally Responsive Polymer Electrolytes,” *Advanced Materials*, vol. 24, pp. 886-889, February 2012.

D. Jiao and S.B. Rempe, “CO₂ Solvation Free Energy using Quasi-Chemical Theory,” *Journal of Chemical Physics*, vol. 134, p. 224506, 2011.

Radionuclide Transport from Deep Boreholes

141668

Year 3 of 3

Principal Investigator: P. V. Brady

Project Purpose:

Disposal of deep (>3 km) boreholes could be a relatively inexpensive, safe, and rapidly deployable strategy for disposing America's nuclear waste if: 1) the thermal-hydrologic-chemical-mechanical (THCM) controls over borehole stability and radionuclide transport up/along the borehole and through salinity-stratified groundwater could be predicted with sufficient confidence, 2) borehole backfills and seals could be designed to provide intrinsic chemical and physical resistance to the movement of water and long-lived radionuclides, including the most mobile isotope of concern, iodine-129. While suitable crystalline host rocks are ubiquitous throughout the country and the technology for drilling deep boreholes is reasonably common in the oil and gas industry, the fundamental science of borehole stability and borehole chemical transport is lacking.

We will build the fundamental science of borehole stability and chemical transport by: 1) developing a "first-of-its kind" coupling of THCM codes that can predict mechanical stability, heat flow, fluid movement, and chemical transport under borehole conditions, and 2) establishing the experimental and theoretical basis for optimizing borehole seals and backfill design to limit vertical transport of radionuclides up the borehole. These efforts will be used to advance a reference design and pilot testing approach for deep borehole disposal of nuclear waste.

Summary of Accomplishments:

1. We completed the borehole reference design.
2. We completed a draft of the site characterization report.
3. We presented new thermal calculations at the International Geologic Congress in Australia. These calculations indicate the following: 1) thermal-hydrologic modeling shows limited groundwater circulation from waste heat. This suggests that radioactive waste would be effectively isolated from the biosphere, 2) the reference design and operations for a deep borehole disposal system based on current drilling methods and engineering technology suggests that deep borehole disposal is viable and cost effective, and 3) assuming fuel assemblies are dismantled and consolidated, the disposal capacity of each borehole and a reasonable estimate of the number of boreholes required suggests that the deep borehole disposal concept would have sufficient capacity to deal with America's nuclear waste problem.

Significance:

We advanced the frontiers of engineering by developing the reference borehole design. We aided energy security by showing that deep boreholes are viable disposal sites for radioactive waste, and by informing policy makers (e.g., the Blue Ribbon Commission on America's Nuclear Future [DOE]) of the option.

Transportation Energy Pathways

141670

Year 3 of 3

Principal Investigator: T. H. West

Project Purpose:

In the coming decades, personal transportation options and the required infrastructure must undergo a fundamental transformation to achieve the nation's economic, environmental, and national security needs. New fuel sources, stronger consideration of greenhouse gas emissions, and application of new technologies will contribute to this transformation to sustainable transportation solutions. Moreover, the heterogeneous distribution of potential resources and populations suggests that the US should consider regional transportation energy systems rather than monolithic national architectures. The complexities and unintended consequences of such a multi-pronged approach are not well understood, e.g., how can mixes of energy sources and improved efficiency standards fit together into secure, robust, and sustainable solutions? What technological innovations will be needed? Systematic, dynamic, integrated analysis methodologies and tools are needed to understand the complex transformation from the current petroleum-based transportation system to one that incorporates alternative fuels and electric vehicles.

This project is developing an Energy Pathways Model (EPM) of regionally deployed transportation systems for a representative set of future transportation energy sources, technologies, and demands. The EPM is unique in its comprehensiveness and its ability to analyze the time-evolution of technological development across multiple transportation energy systems. By considering the complex interrelationships of potential transportation energy systems, this capability enables assessments of the synergies and potential of these systems, identification of technological gaps, and compatibility with the current and future vehicle fleet. This project is creating a modular transportation energy pathways analysis methodology that can be continually expanded and improved to provide an enduring capability to answer the transportation energy questions of highest importance to the nation. The EPM will provide a foundational tool for Sandia's transportation energy strategy, will enable Sandia and its partners to assess technology gaps with the highest risks/rewards, and will identify key issues and constraints in transitioning to future transportation energy mixes.

Summary of Accomplishments:

We developed a system dynamics based model of the supply-demand interactions between the light duty vehicle (LDV) fleet, its fuels, and the corresponding primary energy sources. The differentiating feature of this model is the ability to conduct global sensitivity and parametric trade-space analyses. This model incorporates consumer choice between competing vehicle drivetrains and breaks vehicles into different size classes, based on feedback from our auto industry partners. The model also includes the dependence of regional recharging/refueling infrastructure development on market penetration of the corresponding vehicle drivetrains. The model has different energy supply curves, electricity generation mixes, fuels costs and availabilities, vehicle mixes, and consumer choices in each state.

During the past year, we completed a significant milestone on the project, the publication of our model and analysis results in a peer-reviewed publication (*Energy Policy*). Key findings in this paper include: electric vehicles alone cannot drive compliance with the most aggressive greenhouse gas (GHG) emission reduction targets, even as the current electricity source mix shifts away from coal and towards natural gas. Since internal combustion engines will comprise the majority of the LDV fleet for up to forty years, conventional vehicle efficiency improvements have the greatest potential for reductions in LDV greenhouse gas emissions over this time.

This project has led to two follow-on projects with the DOE Energy Efficiency and Renewable Energy's Vehicle Technologies Program and the DOE Clean Energy Research Center. These efforts include additional analyses and extensions of the model beyond the scope of this project.

Significance:

America's national security is increasingly dependent on its access to reliable, clean, and affordable energy. This project provides a foundational tool for Sandia's transportation energy strategy, and will guide future technology assessments by identifying technology gap areas with the highest risks/rewards. For DOE's Office of Energy Efficiency and Renewable Energy, US industry, and others, the capability developed in this project enables exploration of options to enable national transportation infrastructure transformation. The capabilities built through this effort will be global in nature and can be tailored for international analyses, providing Sandia with opportunities to impact global transportation energy development.

Refereed Communications:

G.E. Barter, D. Reichmuth, J. Westbrook, L.A. Malczynski, T.H. West, D.K. Manley, K.D. Guzman, and D.M. Edwards, "Parametric Analysis of Technology and Policy Tradeoffs for Conventional and Electric Light-Duty Vehicles," *Energy Policy*, vol. 46, pp. 473-488, July 2012.

Development of First-Principles Methodologies to Study Electro-Catalytic Reactions at Metal/Electrolyte Interfaces

141927

Year 3 of 3

Principal Investigator: B. Debusschere

Project Purpose:

Electrochemical processes at metal/electrolyte interfaces are the basis of many devices facilitating conversion between different forms of energy such as solar, electrical, and chemical. For example, fuel cells, electrolyzers, and batteries are used for conversion between chemical and electrical energy. While these devices vary widely in terms of operating conditions, materials composition, and energy input, the performance of the devices is primarily governed by similar molecular electrochemical transformations involving transfer of charged species across metal/electrolyte interfaces. These critical electrochemical transformations are poorly understood and difficult to probe with conventional experimental tools as the metal/electrolyte interfaces are hidden and inaccessible to the experimental probes.

This project, in collaboration with the University of Michigan, employs quantum density functional theory (DFT) calculations and ab-initio metropolis (MMC) and kinetic Monte Carlo (KMC) simulations to study elementary step mechanisms of electro-catalytic reactions on electro-chemical devices. We employ realistic model systems that account for the presence of the metal/electrolyte interface. Potential bias and electric field effects are incorporated in our first principles calculations. We are focusing on the underlying electro-chemical transformations governing the processes of oxygen reduction reaction (ORR) and oxygen evolution (OER) at metal/electrolyte interfaces in electrolysis devices and lithium/oxygen batteries. While we focus on these particular transformations, the developed methodology is universal, and can be easily employed to other electro-catalytic systems where electrolyte/metal interfaces electrochemistry plays a role, such as solid-state sensors, microelectronic devices, solid-state batteries, fuel cells and many others.

The proposed theoretical framework will allow us to obtain molecular information that is virtually impossible to obtain through other means. The project will, on the one hand, advance our ability to model molecular electro-chemical transformation from first principles and, on the other hand, provide us with molecular information that is critical for the formulation of superior new materials for electrochemical transformations, including materials for fuel cells, electrolyzers, and batteries.

Summary of Accomplishments:

Building on our general framework developed in FY 2010 - FY 2011 for studying electrochemical transformations at solid/electrolyte interfaces, we continued our analysis of the oxygen evolution/reduction reactions in lithium/oxygen batteries and added an analysis of oxygen species under relevant catalytic conditions for ethylene epoxidation.

Two barriers to lithium/oxygen battery technology are associated with the loss of capacity between discharge cycles and sacrificing potential to drive the oxygen evolution reaction (Li-OER). Our analysis, therefore, focuses on this reaction, but our approach also addresses the complementary discharging oxygen-reduction reaction (Li-ORR). Literature identifies a few materials such as gold and platinum that bind oxygen in a balance between weak and strong binding that allows the use of these catalysts for lowering both charging and discharging losses. We began developing a model system for investigating the solid/solid interface of lithium peroxide and catalyst surface.

In heterogeneous catalysis, oxygen can adsorb to catalytic surfaces in different states (i.e., electrophilic, nucleophilic, neutral) and drive both desired and undesired reactions. The electronic fingerprint of these

states are easy to identify using the shift in the binding energy of their core electrons but the exact geometry (e.g., surface oxygen, oxygen adsorbed at under-coordinated step/edge sites) remains unclear. Our ultimate objective is to establish a direct connection between the geometric and electronic structure of surface oxygen species on Ag (silver) surfaces under relevant catalytic conditions and how it relates chemical and catalytic activity. Establishing such a connection is critical for the characterization of various oxygen species that exist on the surface of Ag during catalytic oxidation reactions. At this point, the geometric structure of the relevant, catalytically active oxygen atoms on Ag surfaces is unknown. Various structures have been proposed based on the analysis of the electronic fingerprint associated with active oxygen atoms and we propose to directly link these two analyses.

Significance:

The developed methodological framework is universal and can be easily employed to address other electro-catalytic systems, such as solid-state sensors, microelectronic devices, solid-state batteries, fuel cells, and many others. This ability will allow us to discover and engineer novel materials for electrochemical conversion through more systematic knowledge-based approaches. This supports the DOE missions in terms of better science; predictive science-based design driving improved energy efficiency, reduced pollution, and enabling renewable energy technologies. This will facilitate better environmental stewardship, and support DOE's national security goal by reducing the dependence on (foreign) fossil fuels and reducing the impact on climate change.

Effect of Doping on the Performance of Solid-Oxide Fuel Cell Electrolytes Produced by a Combination of Suspension Plasma Spray and Very Low Pressure Plasma Spray 141929

Year 3 of 3

Principal Investigator: A. C. Hall

Project Purpose:

Plasma spray coating techniques allow unique control of electrolyte microstructures and properties. This can enable significantly improved solid oxide fuel (SOFC) designs. However, electrolytes deposited using conventional plasma spray have high porosities and cannot be applied in thin layers ($<50\text{ }\mu\text{m}$). A solution to forming thin, dense electrolytes of ideal composition for SOFCs is being explored by combining suspension plasma spray (SPS), a new spray technique being developed at Purdue University, with very low pressure plasma spray (VLPPS) equipment available only at Sandia's Thermal Spray Research Laboratory (TSRL). SPS involves feeding a solvent-based suspension of submicron powders into a plasma torch. The solvent is evaporated, the powders are melted or vaporized, and propelled toward a substrate. Liquid and vapor phase deposition of the feedstock forms the coating. Purdue introduced this technique to Sandia.

Oxygen ion conductivity can be optimized using suspension plasma spray. Purdue has shown recently that dopant compounds dissolved in the suspension are incorporated into the coating during plasma spraying. Thus, it is possible to change the chemistry of the feedstock during deposition. We have demonstrated the ability to quickly and systematically change the composition of the sprayed SOFC electrolyte. This allows optimization of its oxygen-ion conductivity by simply adjusting the suspension composition. This project is systematically exploring electrolyte doping and its influence on the performance of an SOFC system. Once the doped suspension is plasma sprayed, the electrolyte/coating will be characterized at Purdue as part of an SOFC system.

Summary of Accomplishments:

This project advanced Sandia's capability in the area of very low pressure plasma spray (VLPPS) and suspensions plasma spray (SPS). This coating technology is still emerging, however, we have demonstrated the ability to prepare coatings in thickness/density regimes not currently accessible with conventional thermal spray or thin film processes. Specifically, our ability to effectively prepare dense ceramic coatings in the 1–10 micron thickness regime using suspension feedstock has been improved.

By combining SPS with VLPPS, thin and dense electrolytes of appropriate composition for SOFCs were prepared. By working at pressures as low as 2.4 Torr, energy partitioning in the plasma and its interaction with the surrounding chamber atmosphere was dramatically reduced. The result was a significant increase in plasma mean free path length and plasma velocity. This caused the plasma to remain coherent longer and deposit uniformly over larger areas. It also increased the total time particles were entrained in the plasma and consequently the amount of energy these particles absorbed. The increased residence time in the plasma resulted in scandium dopant atoms being incorporated into the coating. No scandium oxide peaks were present in x-ray diffraction (XRD) of the coating, indicating that scandium oxide is not present in the finished coating. Nevertheless, chemical analysis Energy Dispersive Spectrometer (EDS) confirmed the presence of Scandium in the coating. This suggests that Scandium atoms have been incorporated into the Zr_2O_3 coating material.

These data shows that compounds dissolved in the suspension (i.e., dopants) are incorporated into the coating during plasma spraying. Thus, it is possible to change the chemistry of the coating material by changing the composition of the liquid medium used to create the powder suspension. This means that it

is possible to quickly and systematically change the composition of the sprayed coating by simply adjusting the suspension composition.

Significance:

The ability to change the composition of a coating by changing suspension composition provides a straightforward, controllable mechanism for preparing unique coatings and thermal spray feed stock powders. This capability gives Sandia increased flexibility to design unique materials needed to meet its diverse national security missions, particularly with respect to DOE's energy security mission, specifically, alternative energy initiatives in the area of fuel cells. The improved understanding of the VLPPS/SPS process gained through this fuel cell development project has increased our ability to successfully prepare VLPPS coatings.

Refereed Communications:

J.D. Fleetwood, R.W. Trice, E. Slamovich, A. Hall, and J. McCloskey, "Solid Oxide Fuel Cell Electrolytes Prepared by a Combination of Suspension Plasma Spray and Very Low Pressure Plasma Spray," in Proceedings of the 2012 International Thermal Spray Conference, 2012.

M.F. Smith, A.C. Hall, J.D. Fleetwood, and P. Meyer, "Very Low Pressure Plasma Spray—A Review of an Emerging Technology in the Thermal Spray Community," *Coatings*, vol. 1, pp. 117-132, 2012.

Guiding Options for Optimal Biofuels

148066

Year 3 of 3

Principal Investigator: S. M. Paap

Project Purpose:

It is widely recognized that current biomass-derived transportation fuels, especially corn-derived ethanol, suffer from a number of shortcomings, including incompatibilities with existing vehicles and infrastructure, resource-intensive production methods, and low energy densities. It is also increasingly well recognized that any sustainable biofuels solution will be highly region-dependent due to differing feedstock growth conditions and available infrastructures. A key, missing piece in our understanding is how to integrate these sometimes-competing considerations in order to enable large-scale deployment of biofuels in a responsible manner.

The complex problem of selecting an optimal biomass-derived transportation fuel requires physically relevant, yet computationally manageable models that adequately represent the main processes driving the overall system. These components are currently lacking. This project will help close this critical gap by developing simplified models representing the conversion of the biomass feedstocks to liquid transportation fuels. These simplified models will then be incorporated into a multiscale and multidomain model framework that couples the selection and development of feedstocks and conversion processes to provide a basis for exploring the entire pathway from agricultural inputs to the end use of the fuel.

The project looks beyond existing technologies and infrastructure in order to probe the fundamental constraints and trade-offs affecting the deployment of biomass-derived transportation fuels. The real innovation here lies in the multidisciplinary integration across temporal, spatial, and conceptual scales that will result in a unique modeling framework that leverages Sandia's strengths in systems modeling and analysis in a way that informs better decision making with sparse and/or uncertain data inputs. We seek to ultimately gain valuable insight into what a future biofuels solution could and should look like.

Summary of Accomplishments:

During the course of the project, we developed a modular, flexible modeling and analysis approach that is well suited for the evaluation of early-stage technologies and processes to convert biomass to liquid transportation fuels. Our approach connects simplified models of individual process units in a unified framework, enabling the representation of multiple pathways from biomass to liquid fuels and accounting for the inherent uncertainty in process inputs and performance through the use of Monte Carlo analysis techniques. The modeling framework is general and flexible enough to readily incorporate advances in technology across the entire process, while still representing the important physical processes that govern the behavior of the system.

The modeling framework was applied in a comparative analysis of biochemical pathways to convert switchgrass to either ethanol or fatty acid ethyl ester (FAEE), leveraging connections between Sandia and the DOE's Joint BioEnergy Institute (JBEI) to ensure that our work reflected state-of-the-art knowledge of advanced technologies being applied to the production of biofuels. Our results highlight the key drivers and trade-offs that determine the performance of the competing pathways in terms of relevant economic and environmental metrics, and challenge widely held assumptions regarding the relative advantages and disadvantages of processes to produce ethanol and so-called advanced biofuels in general. These conclusions were incorporated into a high-impact manuscript that has recently been accepted for publication in the peer-reviewed journal, *Biomass and Bioenergy*. Our analysis offers

concrete paths to process improvement, and provides valuable insight to the level of improvement that can be expected in terms of the metrics of interest.

Beyond the current project, this modeling framework may be expanded to incorporate new conversion process pathways. In FY 2012, it formed the foundation of a new study of biomass-derived jet fuel production supported by Lockheed Martin Joint Vision funds.

Significance:

The modeling and analysis approach developed during the course of this project directly supports the energy security mission of the DOE and Sandia by delivering capabilities which offer insight into the most promising pathways to large-scale deployment of reliable, clean, and affordable biomass-derived transportation fuels. The project enhances the impact of science and technology innovations by identifying high-potential biofuels research areas to more effectively leverage resources in support of this mission.

Refereed Communications:

S. Paap, T. West, D. Manley, E. Steen, H. Beller, D. Dibble, S. Chang, and B. Simmons, “Biochemical Production of Ethanol and Water-Immiscible Biofuel from Lignocellulosic Biomass: A Comparative Analysis of Environmental and Economic Performance,” to be published in *Biomass and Bioenergy*.

CO₂ Reuse Innovation — Novel Approach to CO₂ Conversion using an Adduct-Mediated Route

151300

Year 2 of 3

Principal Investigator: R. Kemp

Project Purpose:

The need to convert “useless” carbon dioxide (linear CO₂) into valuable products is of high interest worldwide. Performing this process at as low a temperature as kinetically possible is also advantageous, as it minimizes the energy input into the system as well as lowers the possibility for undesired side reactions. In order to achieve success, it is necessary that Sandia explore multiple routes to CO₂ capture and fixation. We have recently prepared complexes that form CO₂ “adducts” with inexpensive, plentiful main group elements such as tin and zinc. Interestingly, the CO₂-fragments in these metal adducts are now bent significantly from linearity in the solid-state crystal structures. We hypothesize that given the correct combination of metal and ligand structures the “bent” CO₂ molecule will be easier to either chemically or electrochemically reduce to organic products. If demonstrated, this is game-changing technology for DOE and Sandia. However, improvements in moisture and thermal stability of the various organometallic complexes are required in order to produce organic products. We are examining various valence-active main group metals with low-to-high electron counts to determine which metals most effectively transfer electrons into the CO₂-framework. These electrons can be provided either electrochemically or chemically with appropriate reducing agents. Key within our research plan is an evaluation of the role of each specific reductant. The nature of the metal-ligand interaction (sterics and electronics) is also being studied experimentally and computationally, because understanding the stability of this combination is critical to scientific advancement. Additionally, this knowledge will be of interest to other DOE-funded catalysis projects. Ligands have been synthesized this year to minimize sensitivity to protic-containing solvents or reagents. From these individual component studies, an entire catalytic system will be designed and chemically constructed to evaluate the hypothesis that chemical or electrochemical reduction of CO₂ can be facilitated by main group metal adduct formation.

Development of Alkaline Fuel Cells

151301

Year 2 of 3

Principal Investigator: M. Hibbs

Project Purpose:

This project focuses on the development and demonstration of anion exchange membrane (AEM) fuel cells for portable power applications. For fuel cells to meet the needs of consumer electronics, significant reductions in cost are required. To meet demanding DOE portable power targets, radical approaches need to be considered. AEM fuel cells differ from proton exchange membrane (PEM) fuel cells primarily in that the operating environment is alkaline rather than acidic. AEM fuel cells offer huge potential to reduce cost and enable significant system simplification because they operate at pH conditions where non-precious catalysts are stable and highly performing (comparable to platinum). Additionally, the ability to operate in high pH increases the number of fuel choices (alternative fuels) available and increases the efficiency of the electrochemical oxidation process. For historic reasons, these systems have not been strongly pursued, largely because they were believed to be limited by relatively poor stability and low conductivity of the membrane material and the difficulty involved in fabricating membrane-electrode assemblies from these materials.

This project would leverage recent breakthrough performance of AEMs developed at Sandia and electrocatalysts developed at the University of New Mexico to develop alkaline fuel cells with state-of-the-art performance and durability results.

Mass transport within the electrodes is critical to performance and yet, no electrode architecture has been specifically tailored and optimized for use in an AEM fuel cells. Because Sandia has developed cationic polymers for AEMs and which can also be dissolved in solvents such as alcohols, we are in a unique position to work with catalyst developers to experiment with the design of electrodes for AEM fuel cells.

Constitutive Framework for Simulating Coupled Clay/Shale Multiphysics 151302

Year 2 of 3

Principal Investigator: F. D. Hansen

Project Purpose:

This research intends to place the modeling capability of Sandia's Sierra codes at the forefront of technical applications pertaining to clay and tight shale geologic formations. Over the past 12 months, this effort has resulted in numerous advances, and we are on target to develop and demonstrate this modeling capability. The research effort has included significant experimental success on radionuclide sorption in clay and clay-bearing sediments and continuous development and validation of the constitutive relationships.

A series of experiments was completed to characterize the clay minerals being used and iodide uptake. Seven clay minerals were characterized for nitrogen adsorption and methylene blue surface areas, and cation exchange capacity. Iodide uptake was measured in batch systems using an experimental matrix of ionic strengths and compositions and under variable pH conditions. The combined experimental outcome led to the discovery of a novel iodide uptake pathway distinct from classical surface chemistry descriptions of ion exchange or surface complexation. We are currently developing a consistent thermodynamic framework of iodide behavior under all conditions. The next stage of experimentation examines iodide diffusion in clay systems relevant to waste disposal. The high-pressure system used to confine the clay has been configured and initial experiments are under way at ~70 bar with anticipated higher pressures in future experiments.

Working with Texas A&M University (TAMU), we have implemented the Double Structure-Barcelona Basic Model (DS-BBM) in the Sierra/Mechanics constitutive model library. We have tested the implementation of the model using the Sierra/Mechanics code, Adagio, under isothermal conditions that involve wetting/drying and externally applied stresses. The internationally recognized finite element code CODE_BRIGHT was used to verify that the model is implemented and working correctly. We are evaluating the DS-BBM in a more complex coupled thermal-hydraulic-mechanical model (THM) of the Full-Scale Engineered Barrier Experiment (FEBEX) mockup using the Sierra/Arpeggio coupling of Aria and Adagio.

In-Situ Diagnostics for Fuels Model Validation with ACRR 151303

Year 2 of 3

Principal Investigator: D. Fleming

Project Purpose:

In order to support fuels development work for advanced nuclear reactors, numerous computational models are being developed at Sandia and elsewhere. These codes aim to model the behavior of radiation-damaged materials, including the fuel and cladding, with increased fidelity over current models. Benchmark experiments are recognized as providing essential data to validate the computational models.

While the ultimate goal of these modeling efforts is to have validated codes to predict fuel performance, the current development efforts have focused primarily on code development. A reactor-scale experimental program to provide detailed validation data for current and proposed new fuel compositions during reactor transients is not currently under way. Fuel disruption tests performed at Sandia during the 1980s obtained visual data, but no model validation data. Therefore, an opportunity exists to develop an experimental program for Sandia's Annular Core Research Reactor (ACRR) with the goal of providing quantitative validation data during transient conditions for developing computational codes.

We are using the ACRR to perform small sample, separate effects, irradiation studies during reactor transients, with the goal of developing benchmark experimental results (i.e., time dependent, 3D clad strain) to be used in fuel/cladding modeling codes (i.e., the Sandia Material Point Automated Lagrangian Eulerian ([MPALE]) code. Our team is establishing a baseline non-fueled test capability and developing the experimental program, including required ES&H plans, to obtain the data. We will then begin evaluating in situ diagnostic techniques, such as digital image correlation or advanced strain gauges, on non-fuel items in ACRR to validate the experimental technique and quantify experimental uncertainty. We envision using pressurized cylinders made from fuel clad for this phase. We will establish partners to provide fuel pin samples and post irradiation examination (PIE). The final year would be used to perform fueled experiments. These will measure the clad strain of a fuel pin during a transient event to validate Sandia's computational models.

Tier 2 Development of Sandia's Air Bearing Heat Exchanger Technology 151304

Year 2 of 3

Principal Investigator: J. P. Koplow

Project Purpose:

The work is aimed at transforming a recent conceptual breakthrough in air-cooled heat exchanger technology to a TRL-level-4-to-5 technology appropriate for energy sector applications. Limited work conducted to date indicates that the new mechanism for heat transfer proposed for Sandia's Air Bearing Heat Exchanger is potentially a revolution in heat transfer technology. But this new technology is in its infancy. The technical challenges we face include: a) moving far beyond our current rudimentary understanding of the complex fluid dynamic phenomena that govern device physics, b) developing an engineering methodology for global optimization of the ten design parameters that govern device performance, and c) in support of the above goals, development of a computationally tractable fluid dynamic model that is closely coupled to experimental diagnostics such as de-rotated flow imaging, de-rotated thermal imaging, and acoustic spectral correlation. The research is cutting edge in that the air bearing heat exchanger device architecture is a radical departure from conventional air-cooling technology, whose development stagnated in the 1960s. The enormous potential of air bearing heat exchanger technology was recently demonstrated in the laboratory; we measured a heat transfer film coefficient of $120 \text{ W m}^{-2} \text{ K}^{-1}$ in our version 1 prototype device, a factor of ~ 30 improvement relative to a traditional fan-plus-finned-heat-sink device. There is, however, significant uncertainty regarding successful transformation of this new heat transfer mechanism observed in the laboratory into a technology base capable of providing large efficiency improvements ($\sim 30\%$) in applications such as air conditioning, heat pumps, and refrigeration equipment. But given that such cooling loads currently account for 30% of US electricity consumption, it is imperative that we grapple with the numerous technical challenges that must be overcome to realize the potential of Air Bearing Heat Exchanger Technology in real-world applications.

Fundamental Study of CO₂-H₂O-Mineral Interactions for Carbon Sequestration, with Emphasis on the Nature of the Supercritical Fluid-Mineral Interface

151305

Year 2 of 3

Principal Investigator: C. R. Bryan

Project Purpose:

Carbon sequestration via underground storage in geologic formations is a proposed approach for reducing industrial CO₂ emissions. There is a direct need by operators/regulators for better, informed models that incorporate coupled multiphysics processes arising from subsurface CO₂ injection and storage. However, current models do not consider processes at the supercritical CO₂ (scCO₂)-mineral interface and their potential effects on long-term subsurface CO₂ storage. Interfacial processes control the wetting properties of minerals and the chemical reactivity at the scCO₂-mineral interface. The interface properties will be strongly dependent upon the activity of water in the supercritical fluid, which will change as initially anhydrous scCO₂ absorbs water from formation brine. As scCO₂ water activity increases, the water layer on hydrophilic mineral surfaces will thicken, with concomitant changes in surface properties that will affect how scCO₂ wets mineral surfaces, reservoir/caprock hydrological properties, and the mobility of scCO₂. Capillary condensation of water from scCO₂ and coalescence of water films may also occur. Moreover, the development of a water layer may be critical to mineral dissolution reactions in scCO₂, and may affect attractive forces between clay particles. Data are currently lacking to incorporate these processes into models for CO₂ sequestration.

We are developing key theoretical, experimental, and modeling capabilities for understanding the interactions of supercritical CO₂-H₂O fluids with geologic formations. Inherent technical challenges exist in performing nanoscale studies of the scCO₂-mineral interface, and in upscaling nano/core-scale results to reservoir-scale processes. We are using innovative high-pressure spectroscopic methods to evaluate the scCO₂-mineral interface, and will develop methods for evaluating formation of surface water films in scCO₂ and their effect on rock hydrologic properties. This research will provide improved constitutive models and needed experimental data for evaluating and validating the long-term performance of subsurface CO₂ storage.

Development and Deployment of a Field Instrument for Measurements of Black Carbon Aerosols

151307

Year 2 of 3

Principal Investigator: H. A. Michelsen

Project Purpose:

Atmospheric black carbon (BC) consists of combustion-generated soot incorporated into atmospheric aerosols. BC particles strongly absorb solar radiation, and the resulting global warming and regional climate effects are substantial. Brown carbon (BrC) particles are predominantly composed of semi-volatile combustion byproducts and are also suspected of having similar climate effects. In the Arctic, soot settles on snow, decreasing its albedo and leading to melting and further warming. Additionally, aerosols influence cloud properties, leading to large uncertainties in climate models. The physical characteristics of atmospheric particles and the magnitude of their climate effects depend on where they originate, how they mix in the atmosphere, and how their properties evolve as they age. Developing a better understanding of, and parameterizations for, these processes will narrow the uncertainties in climate models. Furthermore, because their physical characteristics depend on their origins and histories, the composition and partitioning among aerosol types can be used as tracers to attribute sources of greenhouse gases (GHGs) for climate treaty verification. BC and BrC particles are small and highly variable in composition and structure; however, existing instruments are incapable of characterizing them with sufficient sensitivity, specificity, and time response to classify populations of particles in air masses. Aerosol mass spectrometers can speciate particles with sufficient sensitivity but do not provide optical information. Filter techniques are too slow. Current optical techniques provide optical parameters but lack specificity. The purpose of this project is to develop a technique and build a field instrument that will simultaneously provide information about particle composition and optical properties. The technique involves implementation of laser-induced incandescence (LII) to quantify the black-carbon component. Highlights of this year's work include: 1) design and construction of a low-loss particle detection cell, 2) development of a new calibration source, and 3) discovery of a new phenomenon in LII of coated particles.

Simulation of Component Transport and Segregation in Nuclear Fuels 151310

Year 2 of 3

Principal Investigator: V. Tikare

Project Purpose:

This project seeks to develop a model that can treat microstructural changes that are driven by both structural features (curvature of the interfaces, interfacial energies, etc.) and chemistry (changing local chemistry due to fission, temperature gradients, etc.). The two, structure and chemistry, are often interdependent. Current models can treat either structure-driven processes or chemistry-driven process. We have developed a model that combines elements from the two leading materials models, the Potts Monte Carlo model and the phase-field model, into a hybrid model that can treat both structure- and composition-driven materials processes. This is the first model that will simulate the coupled processes rigorously. A challenge that was overcome this year involved the fact that the two models are inherently different in the way they treat dimensional quantities, length, time, and energy. We have converted both model components to dimensionless quantities, so that they can treat real materials systems. A further development that is currently being investigated is the use of free energies directly in the phase-field portion rather than the traditional free energy functional that is used to define interfaces. We restrict the use of the Potts feature identification to define the interface and only use the bulk free energy of the phase-field model. Development of the hybrid capability has enabled subsequent simulation of host of materials and processes that are technologically important. The model development in this project is fundamental development of a class of models and is not specifically applicable to a particular materials technology. However, we concentrate on nuclear materials technologies, in particular component and fission product transport and segregation in nuclear fuels. These materials systems were chosen because they are complex and couple the physics of interest. The further developed portion will be useful for hydride precipitation in zirconium-based claddings.

Development of a Modeling Framework for Infrastructures in Multi-Hazard Environments

151313

Year 2 of 3

Principal Investigator: D. A. Jones

Project Purpose:

The continuous operation of infrastructure systems is critical to societal welfare. Currently, much of the protection planning against natural hazards and terrorism is done separately for each infrastructure and each hazard. With limited funding, it is important to balance expenditures for terrorism and natural hazards based on potential impacts.

The key S&T problem is creating a modeling framework for investment planning in interdependent infrastructures focused on multiple hazard risks including terrorism. To develop this modeling framework, three modeling elements must be integrated, as follows:

1. Sophisticated modeling of natural hazards and terrorism: for natural hazards, this includes the ability to specify a number of events (as well as their probabilities of occurrence) that are consistent with the regional hazards.
2. Sophisticated modeling of the terrorist's goals and actions; this representation should admit a range of assumptions about what the terrorist knows and how they identify what to target, given their resource limitations
3. Sophisticated models of interdependent infrastructures are needed in order to predict the impact of specific terrorist attacks and natural hazard events, as well as how the performance of these systems would change based on investments. The tools developed will be applicable across a wide range of infrastructures (DHS, DoD) though we initially focus on electric power and its connections to transportation. We are also explicitly identifying and illustrating methods to validate each element of the framework.

The success of this project rests on our ability to effectively integrate investment planning with game theory. Since natural hazards do not involve a malicious adversary, the modeling in that area does not have the same complexity (though it is critically important). Global optimization techniques and (non-zero sum) leader-follower assumptions will be used to produce a tractable formulation. The value of such a tool in this area is extremely high.

Energy Security Assessment Tools

151314

Year 2 of 3

Principal Investigator: E. D. Vugrin

Project Purpose:

Energy systems serve a keystone role, as other national critical infrastructure and key resource (CIKR) systems depend on them. Disruptions to this sector can affect civilian and military operations, so energy security assessment methodologies must consider this dependence. Current vulnerability assessment (VA) tools are limited in their ability to evaluate the role of energy security. They focus on the identification of vulnerabilities that are “within the perimeter” and may miss dependencies on civilian CIKRs and cyber components. These methods tend to be asset focused, missing mission dependencies and redundancies. Also, they generally address only protection and do not consider recovery actions. Comprehensive energy security assessment tools must be developed to address these limitations. We will develop the capability to evaluate energy security of military missions through the design of quantitative resilience metrics and systematic characterization of mission dependencies. The capability will enable the evaluation of energy security, provide recommendations for resilience enhancing improvements, and enable cost/benefit analysis of improvement options.

This project will advance the current state of mission assessment tools. Including dependencies on civilian CIKRs will enable the incorporation of novel design basis threats (DBTs), resulting in identification of new vulnerabilities. Identification of connections between missions across the military complex will enable application of enterprise-wide solutions for increasing mission assurance (rather than site-specific solutions). Quantitative resilience methods are rare, and we are not aware of any for military applications (not related to mental health). Development of metrics for military settings will be a significant advance in the resilience community.

This approach will be more complex than existing VA methods. Information necessary for the development of conceptual models will be sensitive and require significant interaction. Adaptation of risk metrics to resilience metrics and evaluation of systems with cross-sector dependencies are known challenges in resilience analysis. The benefit will be a more comprehensive evaluation methodology, improving energy security.

Development of Novel Nanoarchitectures to Enhance High-Temperature Thermoelectric Oxides for Clean Energy Harvesting

151369

Year 2 of 3

Principal Investigator: N. S. Bell

Project Purpose:

This project is focused on the development of thermoelectric oxide materials for the capture of energy from waste heat sources from existing systems. Materials processing to create porous thermoelectric materials will lower the thermal conduction of the active oxide while allowing for electrical conduction, and thereby raise the figure of merit for the existing oxide. The technique for generating the porous ceramics focuses on the creation of nonwoven fiber mats using electrospinning of polymer solutions containing sol-gel precursors. These nonwoven mats are converted to porous ceramics by mechanical pressing and calcinations, leading to bulk wafers with interconnected networks of air (for thermal barrier behavior) and the ceramic, in this case Nb-doped TiO_2 (anatase).

Nanostructured morphologies have been investigated based on fiber alignment, nanotube synthesis, and pressure controlled changes to create mixed granular and ribbon-like morphologies. Studies have been performed to examine the effect on density and fiber morphology as related to the level of pressure applied and time duration, as well as the use of polymer mixtures in the fiber to affect the softening point. The new parallel rotating disc (PRD) method creates highly uniform aligned fibers by electrospinning with greater degree of alignment than other methods in the art. Nb doped TiO_2 materials produced by sol-gel methods exhibit deleterious resistance to electrical conductivity, and alternative thermoelectric materials are under consideration. Multiple material systems have been investigated and show that the SrTiO_3 system doped with Nb or La has promise. There remains a need to improve fiber conductivity in future work. The forthcoming research focus will be on defects, and control over defect structures.

Reconstruction of a High-Resolution Late Holocene Arctic Paleoclimate Record from Colville River Delta Sediments

151370

Year 2 of 3

Principal Investigator: T. S. Lowry

Project Purpose:

Current climatic predictions of anthropogenic global warming indicate that Arctic regions will become warmer and wetter by 2100, and that temperature increases in the northern high latitudes could be as much as 3° to 7 °C. The instrumental record in the Arctic goes back only a few decades, and a paucity of knowledge therefore exists concerning recent and Holocene climate change. It is difficult to determine whether year-to-year weather changes occur due to long-term trends and, in turn, whether those trends are related to changes in atmospheric circulation mechanisms such as the Arctic Oscillation. This study, in collaboration with Texas A&M University, will attempt to differentiate between the effects of long-term climate change and the Arctic Oscillation on changing carbon cycling and storage in Simpson's Lagoon, Alaska by: 1) determining historical changes and making predictions about future changes in the sources and amounts of organic carbon input to the Colville River delta and nearby Simpson's Lagoon in the Beaufort Sea and 2) obtaining a better understanding of changes in terrestrial vegetation of the Colville River watershed over the recent Holocene. Estuarine systems, like the Colville River delta, integrate marine and terrestrial signals, providing a unique study area that is especially applicable to the purpose of this study. Because of this, coastal marine sediments are an excellent recorder of continental climate history, integrating large terrestrial areas, with high sedimentation rates and high preservation of organic matter. The Colville River watershed is unique because the Colville River is the largest river in North America that drains only continuous permafrosted ground and yet, because it is so remote, very few data sets exist. Cores from Simpson's Lagoon were collected in August of 2010 and form a longitudinal transect through the Lagoon, extending east of the Colville River delta.

Probing Surface Phenomena in Elevated-Temperature Energy Materials under Realistic Conditions

151378

Year 2 of 2

Principal Investigator: W. Chueh

Project Purpose:

In one hour, more energy from sunlight strikes the Earth than the amount consumed by the entire planet in one year. As the most abundant energy source, the sun must play a large role in any global-scale renewable energy conversion strategy. However, tapping into this vast resource does not come without challenges. The intermittent and geographically varying nature of solar radiation means that storage and delivery of solar-derived energy are critical steps required for mass utilization. Chemical bonds are one of the most effective mediums for storing energy because of their high energy densities. However, despite the great potential of solar fuels, solar-to-chemical and chemical-to-electricity conversion efficiencies remain low and uncompetitive with those of conventional routes. This project will explore the novel, elevated-temperature materials that can be employed for the efficient production of solar fuel from H_2O and CO_2 (via photo/electrochemical and thermochemical dissociation) and its subsequent conversion to electricity (via fuel cells).

As most chemical reactions are thermally activated, even a modest increase in the operating temperature can produce drastic effects on the rates and reduce or eliminate the use of precious elements. To realize the benefits of higher-temperature processes, the understanding of charge and mass transport at gas-solid interfaces will be advanced using in-situ and in-operando techniques to probe the inner workings of state-of-the-art materials and to use this knowledge to identify new materials that will boost energy conversion efficiencies. This research is conducted by President Harry S. Truman Fellow, William Chueh.

Summary of Accomplishments:

We have successfully developed and employed synchrotron-based x-ray spectroscopy and microscopy to study electrochemical phenomena in electrocatalysts for fuel cells and electrolyzers, and in phase-transforming materials for batteries.

Using ceria-based electrocatalyst as a model system, we employed ambient pressure x-ray photoelectron spectroscopy to study defect thermodynamics on the first few atomic layers of the surface exposed to the gas phase. We observed that the surface defect concentrations, particularly of the localized electrons, differ sharply from that of the bulk. Comparison of the surface to the bulk thermodynamics revealed a significant difference, both in terms of the defect formation enthalpy and the formation entropy. We hypothesized that ease of formation of localized electronic defects on the surface relative to the bulk of ceria may be partly responsible for the high activity for hydrogen oxidation in fuel cells and for water-splitting in electrolyzers and thermochemical cycles.

Turning to batteries, we have successfully carried out quasi-in-situ x-ray microscopy to study phase transformation in lithium iron phosphate positive electrodes—that is, we first charged or discharged the battery to a given state under constant current conditions, rapidly removed the liquid electrolyte to freeze lithium exchange between particles, and then examined them using the x-ray microscope. We spanned the length scales of individual particles as well as the macroscopic electrode ensemble. We imaged approximately 450 individual lithium iron phosphate particles across the thickness of the electrode. We show unambiguously that phase transformation proceeds via the particle-by-particle pathway, rather than via the concurrent pathway as proposed by previous work. In fact, the fraction of particles that are

actively undergoing phase transformation (at 50 % state-of-charge) is remarkably small, only ~ 2 %. A statistical analysis revealed a weak correlation between state-of-charge and particle size, indicating that there is little preference to de-lithiate small or large particles selectively.

Significance:

This work is directly relevant to DOE's mission to provide the science and technology to power the US without contributing to climate change. This project is developing new ways to characterize the electrochemical technologies that will be increasingly relied upon to achieve energy security by efficiently storing and converting energy.

Refereed Communications:

W.C. Chueh and S.M. Haile, "Electrochemistry of Mixed Oxygen Ion and Electron Conducting Electrodes in Solid Electrolyte Cells," *Annual Review of Chemical and Biomolecular Engineering*, vol. 3, pp. 313-341, April 2012.

W.C. Chueh, A.H. McDaniel, M.E. Grass, Y. Hao, N. Jabeen, Z. Liu, S.M. Haile, K.F. McCarty, H. Bluhm, and F. El Gabaly, "Highly Enhanced Concentration and Stability of Reactive Ce^{3+} on Doped CeO_2 Surface Revealed In Operando," *Chemistry of Materials*, vol. 24, pp. 1876-1882, April 2012.

F. El Gabaly, A.H. McDaniel, M. Grass, W.C. Chueh, H. Bluhm, Z. Liu, and K.F. McCarty, "Electrochemical Intermediate Species and Reaction Pathway in H_2 Oxidation on Solid Electrolytes," *Chemical Communications*, vol. 48, pp. 8338-8340, August 2012.

Thermal Transport Properties of Nanostructured Materials for Energy Conversion 151382

Year 2 of 2

Principal Investigator: D. L. Medlin

Project Purpose:

Devices based on composite thin film arrays of nanostructures are of emerging interest for photovoltaic, thermoelectric, and piezoelectric energy conversion. An important factor controlling the efficiency of these devices is the thermal transport properties of the nanostructures. However, the thermal transport properties of such nanostructures are poorly understood because it is inherently difficult to measure them. Key issues of concern include contact resistance, surface roughness, equipment resolution, and processing limitations. Two important questions arise. First, how can the thermal transport properties of nanostructures be rigorously measured? Second, what are the relationships between individual nanostructure properties and the effective properties of a composite thin film?

To address these questions, we are pursuing a comprehensive experimental study of the properties of nanostructured thin films and individual nanowires. We focus on ZnO nanostructures because of the importance of this class of material to emerging thermoelectric and photovoltaic applications. We will use multiple measurement techniques, both optical and electrical, to measure the thermal transport, determining the anisotropic nature of the material properties and investigating differences between discrete nanostructures (e.g., single nanowire) and multiple, interacting nanostructures (e.g., nanowire film). The characterization of novel materials necessitates challenging, cutting-edge, adaptive measurement techniques; the development and application of these techniques will enable realization of novel energy conversion materials. This work is a collaboration with Stanford University.

Summary of Accomplishments:

We analyzed ZnO nanowire electrical resistivity data and modeled electrothermal transport accounting for heat generation at metal-semiconductor contacts, axial thermal conduction, and substrate heat losses. The current-voltage relationships and electron microscopy indicate that sample degradation is caused by the interplay of heat generation at contacts and within the nanowire volume. The model was used to interpret literature data for Si, GaN, and ZnO nanowires. We found that ease of fabrication makes solution-synthesized nanowires promising, but contact resistivity may limit their functionality and impact device performance. Annealing processes to eliminate residual surfactant are particularly limited with ZnO nanowires since an insulating oxide readily forms at the nanowire-metal contact for multiple metals, a process that can be amplified with elevated temperatures. Annealing of these solution-synthesized ZnO nanowire structures with Ti and Ti/Al electrodes showed a reduction in electrical conductivity. This work proposes an electrothermal model, which links current-voltage measurement data to the resulting temperature profile of semiconducting ZnO nanowire devices. The contact resistance of the metal-semiconductor contact leads to heat generation at the contact, which surpasses the nanowire Joule heating. Therefore, the contact heat generation limits the operating range of the nanowire device. This work, therefore, assists with electrothermal nanowire measurements and highlights practical implications of utilizing solution-synthesized nanowires.

Significance:

Control of nanostructures and nanostructure properties is of growing importance in development of advanced functional materials and state-of-the-art devices. Such devices are relevant to national security missions in areas including sensors, advanced electronic devices, and energy conversion. The present work provides fundamental information and methodologies for the analysis of thermal and electronic transport in such nanostructures.

Refereed Communications:

S. LeBlanc, B. Swartzentruber, J. Martinez, G. Christoforo, T. Kodama, and K.E. Goodson, “Nanoscale Manipulation, Heating, and Welding of Nanowires,” *Journal of Heat Transfer*, vol. 134, p. 080910, August 2012.

S. LeBlanc, S. Phadke, T. Kodama, A. Salleo, and K.E. Goodson, “Electrothermal Phenomena in Zinc Oxide Nanowires and Contacts,” *Applied Physics Letters*, vol. 100, p.163105, April 2012.

Optimizing Infrastructure Investments in a Competitive Environment 151411

Year 3 of 3

Principal Investigator: R. L. Chen

Project Purpose:

In many complex systems, individuals/institutions compete for the use of a finite amount of infrastructure capacity (e.g., generation firms compete for transmission capacity). In such systems, the optimization of infrastructure investments must take into consideration competition for the use of infrastructure resources. However, most existing models assume a centralized planning approach where investment decisions are made in a coordinated fashion to maximize social welfare. Such coordinated system models are unrealistic if competition plays a crucial role. In a deregulated electric power industry, for example, generation investment decisions are made by individual institutions with little centralized coordination. These institutions make decisions on the basis of expected future prices and returns on investments. This research develops new models and optimization methods to effectively analyze multilevel Stackelberg games for infrastructure planning, specifically taking into consideration competition (which may be adversarial). These models and optimization methods will allow decision makers to predict the responses of competing individuals to infrastructure investment decisions, analyze infrastructure investment risk, and perform sensitivity analysis. These types of problems often take the form of a tri-level program, in which infrastructure investment decisions are made at the first level. In the second level, infrastructure users compete for the use of limited resources and make investment decisions that maximize their own utility. Finally, at the third level, operating level decisions are optimized based on the investment decisions made in the first two levels. These types of tri-level optimization problem are extremely challenging to solve. Currently, methods based on large-scale decomposition methods reformulate such problems into stochastic programs, with an exponential number of scenarios. Thus, only the smallest instances are tractable. We are developing new models, mathematical programming approaches, and solution strategies (combining large-scale decomposition algorithms with the use of computationally efficient separation oracles) that facilitate efficient solution and rigorous analysis of these types of games.

Summary of Accomplishments:

In FY 2012, we focused on competition that is adversarial (as opposed to market driven). We developed bi-level and tri-level optimization models for infrastructure vulnerability analysis and augmentation. Bi-level and tri-level programs model the decision making of both the infrastructure owner and that of an adversary, who is trying to inhibit infrastructure operations. We developed cutting plane/column generation algorithms, for solving general tri-level optimization problems. We demonstrated via computational experiments, using IEEE test systems, that the new cutting plane algorithms using bi-level separation problems are more than two orders of magnitude faster than the standard decomposition algorithm.

Significance:

This project developed optimization and analysis capabilities that are relevant to the energy security mission of DOE, and to power grid design in particular. In addition, many Sandia, DOE, DoD and Department of Transportation programs will benefit from enhanced capabilities in the analysis of competition and adversaries in hierarchical systems, advancements in computational models, and solution approaches of these hierarchical systems.

Refereed Communications:

R.L. Chen, N. Fan and J-P Watson, “N-1-1 Contingency-Constrained Optimal Power Flow by Interdiction Methods,” in *Proceedings of IEEE Power and Energy Society Conference*, 2012.

R.L. Chen, A. Cohn, N. Fan and A. Pinar, “N-k-Epsilon; Survivable Power System Design,” in *Proceedings of Probabilistic Methods Applied to Power Systems (PMAPS) Conference*, 2012.

Formation of Algae Growth and Lipid Production Constitutive Relations for Improved Algae Modeling

153236

Year 2 of 3

Principal Investigator: P. E. Gharagozloo

Project Purpose:

Algae-based biofuels have generated much excitement due to their potentially large oil yield from relatively small land use and without interfering with the food or water supply. Algae mitigate atmospheric CO₂ through photosynthetic metabolism. Production of algal biofuels will reduce dependence on foreign oil by providing a domestic renewable energy source. Important factors controlling algal productivity include temperature, salinity, and the light-to-biomass conversion rate. Lipids produced by algae are easily converted into various fuels, but they must be generated in large quantities for efficient fuel production. The generation and regulation of lipids in the form of triacylglycerols (TAGs) is not well understood and needs to be studied to determine production levels under various conditions. Parametric studies of lipid-producing marine species, typically serial experiments, that use off-line monitoring of growth and lipid levels, are time consuming and incomplete. These are the necessary precursors for computational models, which currently lack the data necessary to accurately simulate and predict algae growth and lipid production. This project begins with an algae growth and lipid production parametric study. Using innovative techniques to control temperature, salinity, and light within a parallel growth apparatus, we have greatly decreased the time and mass of algae required to obtain fully parameterized growth and lipid formation constitutive relations. The knowledge gained will enable computational models to optimize algae growth in real-world conditions with varying temperature, light, and salinity over the course of a day and year.

Analysis of Gas-Lubricated Foil Bearings in Supercritical CO₂ Flow 153887

Year 2 of 2

Principal Investigator: T. M. Conboy

Project Purpose:

The DOE is currently in development of next-generation nuclear power reactors. In this aim, reactors using a closed-Brayton power conversion cycle have been proposed, which have the potential to achieve higher outlet temperatures, higher thermal efficiencies, and reduced capital cost in comparison to current steam plants. The supercritical-CO₂ (S-CO₂) power cycle has been identified as a leading candidate for this application as it can achieve high efficiency at relatively low operating temperatures, with extremely compact turbomachinery. Progress on S-CO₂ power cycle hardware at Sandia has advanced quickly, identifying areas that will require further R&D; in particular, turbomachinery thrust-bearing performance has proven to be a limitation. This project is therefore carrying out in depth analysis of thrust bearings for application to the S-CO₂ power cycle.

Sandia has been a leader in development of the S-CO₂ cycle, and is in possession of unique facilities for testing of turbomachinery in high-pressure supercritical fluid flow environments. One critical area not fully addressed yet for this technology is an analysis of the hydrodynamic and thermal behavior of the thrust bearings during turbomachinery operation. At present, thrust-bearing performance has proven to be the factor limiting maximum compressor rotation frequency, but is not yet well understood. A model validated by experimental data is necessary for improved understanding of cycle performance.

Summary of Accomplishments:

A two-pronged approach was undertaken to address thrust-bearings issues: First, an aggressive program was implemented to design and test an advanced thrust-bearing type within an S-CO₂ component test facility at Sandia. Under this project, a bearings test facility was built, and advanced bearing type was designed and manufactured. The advanced bearing was tested in S-CO₂, demonstrating that it could support necessary thrust loads at reduced power consumption. Secondly, a computational modeling effort was undertaken to improve understanding of thrust-bearing performance and operational limits. The model was compared to test results with favorable agreement. Modeling results have helped to define a test operating envelope that specify operational limits of the S-CO₂ turbine, preventing bearings damage, and saving money that would otherwise be spent on costly repairs and system downtime. This work taken in its entirety has resulted in a wealth of new understanding of thrust-bearings performance in an S-CO₂ turbine and has produced a number of design recommendations for a next-generation thrust-bearing design for reduced friction and higher temperature capacity. Modeling results indicated that a bearing with smaller diameter and fewer thrust pads could maintain thrust load capacity with reduced frictional losses. In addition, incorporation of geometric features (ex: chevrons) at the trailing edge of each thrust pad to expel hot fluid would likely increase load capacity by enhancing the thermal wedge effect, while improving thermal management. Experimental work also demonstrated that tighter engineering tolerances could be attained by using a stamped manufacturing approach rather than assembling the thrust bearing with many small pieces. Finally, it is also recommended for next-generation bearings to plasma spray the thrust runner with a solid lubricant, and use bare thrust pads. This improvement is directed at increasing the temperature resistance of the current model, which cannot be heated beyond the dissociation temperature of Teflon.

Significance:

The supercritical CO₂ power cycle is applicable to any industry or application that desires compact, high efficiency power systems; this may include nuclear power (stationary, space power/propulsion, naval), fossil (coal, gas turbine heat recovery), solar thermal, geothermal, etc. Advancements to turbomachinery that enable further development of the S-CO₂ power cycle hardware development program therefore have an impact on national security/defense technologies and DOE national energy policy.

Refereed Communications:

T. Conboy, S. Wright, J. Pasch, D. Fleming, G. Rochau, and R. Fuller, "Performance Characteristics of an Operating Supercritical CO₂ Brayton Cycle," *Journal of Engineering for Gas Turbines and Power*, vol. 134, p. 111703, 2012.

T. Conboy, "Real Gas Foil Thrust Bearings Operating in the Turbulent Regime," to be published in the *Journal of Tribology*.

Compact Reactor for Biofuel Synthesis

153889

Year 2 of 2

Principal Investigator: J. W. Pratt

Project Purpose:

Liquid fuels synthesized from renewable CO and H₂ could displace petroleum-based fuels to provide clean, renewable energy for the future. Small scale (<20 bbl/day) reactors for synthetic liquid fuels production are an emerging developmental area that may enable mobile biomass-to-liquids plants suited for on-demand liquid fuel production from diverse, underutilized, local resources.

Fischer-Tropsch synthesis (FTS) is an attractive option in the process of converting biomass-derived syngas to liquid fuels in a small-scale mobile bio-refinery. Computer simulation can be an efficient method of designing a compact FTS reactor, but no known comprehensive model exists that is able to predict performance of the needed nontraditional designs.

The purpose of this work is to enable design of efficient, durable, and flexible small scale and/or novel reactors.

The goal of this work is to create a gas-to-liquids synthesis model with the minimum amount of empiricism and assumptions allowed by the current state of the theory, through integrated physics component models across varying length scales.

Summary of Accomplishments:

This work developed a generalized model framework that can be used to examine a variety of FTS reactor configurations. It is based on the four fundamental physics areas that underlie FTS reactors: momentum transport, mass transport, energy transport, and chemical kinetics, rather than empirical data of traditional reactors.

The model framework was applied to an example application. The general mathematical equations for the underlying physics were not dependent on this application (i.e., not empirical), yet were able to describe the observed phenomena in agreement with literature. The model provided further insight into the process that enabled preliminary design of a novel small-scale reactor that can be analyzed in the same framework.

Significance:

This work addressed a specific need for biomass-to-liquid fuel synthesis as desired by DOE and DoD. The expertise developed over the course of the project is unique at Sandia and can be used not only in this specific application to enhance energy security, but also in other applications where similar integrated physics are encountered. Examples include nuclear weapons design, hydrocarbon reservoir recovery including shale gas, and biological and chemical sensors.

Development of a Raman Spectroscopy Technique to Detect Alternate Transportation Fuel Hydrocarbon Intermediates in Complex Combustion Environments

154319

Year 2 of 2

Principal Investigator: I. Ekoto

Project Purpose:

Existing validation datasets for predictive combustion simulations are incomplete partly due to the inadequate capabilities of currently applied experimental methods. A major gap remains the inability to directly and quantitatively measure hydrocarbon intermediate concentrations more complex than methane, which are necessary to characterize reaction progress variables in more advanced fuels. This gap can be bridged by taking advantage of recent advances in Raman based detection techniques and through the proposed diagnostic developments. The challenge is to differentiate overlapping, temperature dependent Raman spectral signatures from hydrocarbon fuels and their combustion intermediates and convert that information into accurate concentration measurements. Since laminar flame calculations indicate hydrocarbon speciation strongly depends on fuel type and combustion environment, the developed method must be broadly applicable.

Preliminary Raman spectroscopy measurements from laboratory flames of dimethyl ether (DME), a promising alternative transportation fuel, suggest that it should be possible to deconvolve individual spectral contributions from the parent fuel and its main, stable hydrocarbon combustion intermediates and convert this information into quantitative concentrations. Application of this technique, however, requires detailed spectral information about each stable hydrocarbon species and newly developed analysis tools for signal post-processing and data interpretation. For the proposed study, Raman spectral libraries for important hydrocarbon fuels and combustion intermediates have been recorded over a broad range of temperatures using the multiscalar measurement facility located at Sandia, California. Recorded spectra are then converted into synthetic spectral libraries and incorporated into novel spectral analysis models that account for spectral crosstalk from the unknown hydrocarbon concentrations and iteratively find the unknown flame temperature. Performance testing of developed libraries and reduction methods are conducted through an analysis of results from heated mixtures at known compositions and from well-characterized laminar reference flames. The diagnostic represents a first-of-its-kind measurement technique that can be used to temporally and spatially resolve speciated hydrocarbon concentrations during combustion.

Summary of Accomplishments:

Spontaneous Raman spectra for important hydrocarbon fuels and combustion intermediates were recorded over a range of low-to-moderate flame temperatures using the multiscalar measurement facility. Recorded spectra were extrapolated to higher flame temperatures and then converted into synthetic spectral libraries that can readily be incorporated into existing post-processing analysis models that account for crosstalk from overlapping hydrocarbon channel signal. Performance testing of the developed libraries and reduction methods was conducted through an examination of results from well-characterized laminar reference flames, and was found to provide good agreement. The diagnostic development allows for temporally and spatially resolved flame measurements of speciated hydrocarbon concentrations whose parent is more chemically complex than methane — critical data needed to validate increasingly complex flame simulations.

Significance:

Predictive simulation-based design of combustion devices holds the promise to produce cleaner and more efficient engines. Efficiency gains of 20-50% can substantially enhance national energy security while helping mitigate the effects of climate change. However, current predictive simulations offer limited accuracy due to lagging science-based development of simulation submodels, which is hindered by a lack of high-fidelity measurements from well-characterized combustion experiments. This project has enabled enhanced diagnostic capabilities that overcome some of these shortcomings that accordingly benefit the DOE Energy Security and Scientific Discovery and Innovation missions.

Polymer-MOF Nanocomposites for High-Performance Dielectric Materials

155065

Year 2 of 3

Principal Investigator: L. Appelhans

Project Purpose:

Capacitors for power electronics, pulsed power, and energy storage applications require high energy densities, high dielectric breakdown strengths, and high temperature operating capability while maintaining the ability to fail as an open rather than as a short. Current dielectric technologies do not meet these requirements. Energy densities must increase by an order of magnitude in order to satisfy future needs. This goal is impossible to achieve without the development of new dielectric materials. Polymer nanocomposite dielectric materials have demonstrated superior properties relative to dielectrics based on ceramics or polymers alone. However, a major challenge in the development of nanocomposite materials is nanoparticle dispersion. Nanoparticle agglomeration severely diminishes the practical utility of dielectric polymer nanocomposite materials through degradation of dielectric properties and poor reproducibility and scalability. We are exploring the development of polymer nanocomposite dielectric materials with metal organic frameworks (MOFs) as a possible solution to this fundamental problem. MOFs have built in organic moieties on their surfaces that will improve intrinsic particle compatibility with polymers. Furthermore, MOFs have been little studied in terms of electrical properties and there is a wide array of interesting MOFs with promising characteristics. Polymer-MOF nanocomposites provide a very attractive solution to challenges in dielectric development that, if not overcome, will impede the realization of a practical electrical infrastructure

Time-Resolved Broadband Cavity-Enhanced Absorption Spectrometry for Chemical Kinetics

155298

Year 2 of 3

Principal Investigator: L. Sheps

Project Purpose:

Critical experimental measurements of elementary reaction rate coefficients and branching ratios are often impossible because of a lack of adequate detection techniques. Short lifetimes and low concentrations of many reactive intermediates, together with competing reactions and wall effects, impose the following demands on the ideal experimental detection method:

1. Nonintrusive probing of homogeneous reaction zones
2. Simultaneous detection of multiple species, especially important for complex reactions
3. Fast time resolution (typically, better than 10 microseconds) for real-time monitoring of species concentrations
4. High sensitivity (less than 10^{10} molecules/cm⁻³)

Current detection techniques, including conventional absorption or Raman spectroscopy, laser-induced fluorescence, and photoionization mass spectrometry, do not meet all four requirements simultaneously. Furthermore, the technical difficulties are exacerbated at elevated sample pressures: optical detection techniques must contend with broadened and congested spectral features, while mass spectrometric techniques suffer from sample “dilution” effects because of the increased bath gas concentration.

To address this challenge, we are pursuing a general detection method that does fulfill all of these requirements: time-resolved broadband cavity-enhanced absorption spectrometry. This method is inherently in situ and nonintrusive because it relies on optical absorption. Its broadband nature (initially, 300–800 nm) will allow deconvolution of complicated spectral signatures and allow simultaneous kinetic measurements of many species with microsecond time resolution. Lastly, multipass cavity enhancement will yield a substantial (two orders of magnitude) sensitivity increase over single-pass absorption, enough for reliable measurements of reactive intermediates and minor products.

The main challenge of the proposed technique will be careful calibration of detection efficiency and achieving reliable performance over very broad spectral ranges. However, if successful, this method will enable fast, efficient, and reliable measurements in many previously inaccessible systems. It is possible that subsequent extension to the infrared spectral range would enable sensitive time-resolved vibrational spectroscopy in gases and would result in a truly general probe of gas-phase kinetics.

Accelerating the Development of Transparent Graphene Electrodes through Basic Science Driven Chemical Functionalization

155550

Year 2 of 3

Principal Investigator: C. Chan

Project Purpose:

Despite recent intense research on the fundamental properties of graphene, its practical widespread application remains elusive. Graphene has been proposed for use as a transparent electrode owing to the material's high in-plane conductivity, transparency, chemical stability, and elemental abundance. Large interest in this application stems from the desire to replace rare and expensive brittle conducting oxides [e.g., indium tin oxide (ITO)], unstable conducting polymers [(e.g., poly(3,4-ethylenedioxythiophene) PEDOT:PSS)], and fragile optically thin metals as electrical contacts to solar cells, light-emitting diodes, and photodetectors. However, previous efforts in using graphene for electrodes have suffered from poor film quality and uncontrolled interactions between graphene and the contacted materials. Chemical functionalization is a promising means of modifying and improving graphene's interaction with other materials, but current functionalization schemes are not well controlled, characterized, or understood. The practical use of graphene as a transparent electrode material requires control over the chemical functionalization of graphene interfaces, characterizing the physical properties of the functionalized surfaces, and understanding how modifying graphene's chemical nature also affects its material and physical properties.

This work employs a comprehensive characterization methodology to understand the effects of functionalization chemistry on the material and physical properties of graphene. Of particular interest is how chemical functionalization of graphene affects its electronic band structure and its energy band alignment with other materials. These issues, which are still not well characterized or understood in graphene, greatly affect the materials conductivity and transparency, as well as charge injection and extraction in devices. We are initially investigating functionalization chemistries intended to modify the work function of graphene and improve its performance as a transparent electrode in optoelectronic devices. Using knowledge generated from fundamental surface science measurements, and correlating functionalization chemistries to material properties, this work will accelerate the systematic development of optimally functionalized graphene films for transparent electrodes and other applications.

Aerosol Characterization Study using Multi-Spectrum Remote Sensing Measurement Techniques

155804

Year 2 of 3

Principal Investigator: C. C. Glen

Project Purpose:

Atmospheric aerosols affect climate, both directly through scattering and absorption of solar radiation, and indirectly by serving as cloud condensation nuclei or ice nuclei. Because of the complex spatial and temporal variability of atmospheric aerosol, measurements of the vertical structure of physical, chemical, and optical properties are necessary to understand the effects of aerosol concentrations on global climate. Light detection and ranging (LIDAR) remote sensing techniques have been employed to measure the vertical structure of atmospheric aerosol concentrations. However, due to a lack of laboratory comparisons linking LIDAR backscatter to the physical and chemical properties of in situ aerosols, empirical calculations are often used as an intermediary to estimate such properties. Furthermore, the majority of current LIDAR systems only use a few select wavelengths that limit the characterization of the chemical distribution of aerosols present, which directly impacts single scattering albedo calculations, a parameter used by climate modelers. This project is proceeding under the hypothesis that the wavelength specific scattering properties of atmospheric aerosols are strongly dependent on composition. Through the synergy of a multispectral LIDAR and experimental methods, both the particle size distribution and more detailed characteristics of the ambient aerosol particle can be discovered.

By bringing together a multidisciplinary team of researchers, utilizing advanced experimental facilities, and working with powerful computational resources, this work is at the cutting edge of research and development. Detailed future LIDAR retrieval algorithms across a broad range of wavelengths can be developed by using an advanced aerosol chamber coupled with a small multispectral LIDAR system. Through the course of experimental research, there is an associated risk due to the unknown wavelength dependence of the particle backscatter on chemical composition. Therefore, it will be necessary to identify the wavelengths responsible for detailing particle composition. Following completion of laboratory experiments, data will be integrated into an algorithm to measure atmospheric aerosols using an existing Sandia system.

Use of Limited Data to Construct Bayesian Networks for Probabilistic Risk Assessment

156135

Year 2 of 3

Principal Investigator: K. Groth

Project Purpose:

Probabilistic Risk Assessment (PRA) is a fundamental part of safety/quality assurance for nuclear power and nuclear weapons. As energy and defense systems change, PRA must evolve to accommodate technological changes (e.g., digital instrumentation and control automation; passive components), and existing soft-causal risk areas (e.g., aging, common cause failure, human reliability analysis [HRA]). Traditional PRA models are not flexible enough to accommodate these nonbinary soft-causal factors.

Sandia has proven expertise in PRA, HRA, and system modeling, but new knowledge is required to analyze the risks introduced by increasingly complex systems of hardware, software, humans, and organizations. Bayesian Networks (BNs) are a state-of-the-art graphical and mathematical framework that can address these challenges.

BNs are positioned to revolutionize the practice of PRA, but the use of BNs is currently limited to applications where there is substantial statistical data available, or where no data is available; neither of these conditions is common in PRA. In PRA application areas, such as HRA, there is probabilistic information available, but it is in various forms (quantitative, qualitative) and small quantities.

Recently there has been a push to use data to reduce the subjectivity of the HRA models currently used in nuclear power plant PRA. BNs provide the conceptual framework to combine different forms of information, but this has never been done in a PRA application. This work is exploring various sources of data relevant to human performance in nuclear power plants, and explores techniques for synthesizing the information into a BN. This is the first modeling effort of its kind and the resulting model will transform the way that human error probabilities are estimated for PRA.

This work will establish expertise and an analysis capability for construction and use of BNs at Sandia; this capacity is important to maintain Sandia's reputation for and expertise in advanced PRA, and positions Sandia to address the next generation of modeling challenges.

Smart Adaptive Wind Turbines and Smart Adaptive Wind Farms 156702

Year 2 of 3

Principal Investigator: J. White

Project Purpose:

At the end of Q3 2010, the US was the largest producer of wind energy with ~2% of all energy supply coming from wind. Although the percentage is single digit, wind energy is currently the most viable clean energy source and has represented ~40% of all new energy. To improve reliability and efficiency, smart adaptive wind energy plants are needed that have the ability to actively measure and control the magnitude and distribution of forces applied to the rotors and drivetrain in order to maximize performance, minimize imbalance loads, diagnose and regulate the growth rate of damage, and optimize operations and maintenance costs. The proposed work seeks to develop operational monitoring technologies that are the primary requirement in developing smart adaptive wind turbines. Operational monitoring technologies combine sensor measurements with real-time data analysis algorithms to estimate rotor forces and deflections and the state of structural health of the turbine. Current research programs have been focused on the development of component level technology, but have not yet recognized the highly coupled nature of turbine structural dynamics that dictates the need for a unified turbine operational monitoring system.

This work is complex, crosscutting, and forward-looking in nature. Development of this technology is challenging because some critical physical phenomenon in the complex motion of an operating turbine may not yet be modeled. Successful completion of this work will benefit DOE programs, position the laboratory for future funding opportunities, and help establish Sandia as the world leader in operational monitoring. According to the US DOE, *20% Wind Energy by 2030* report, this could lead to a 34% increase in energy capture and a 9% reduction in capital costs.

Fluid Flow Measurement of High-Temperature Molten Nitrate Salts

157145

Year 2 of 3

Principal Investigator: A. M. Kruizenga

Project Purpose:

The specific technical challenge in this project is to design, develop, and characterize unique flow measurement devices that operate up to 700 °C with an error of less than 5%. Current working fluids for concentrating solar power (CSP) applications must achieve very high temperatures, in excess of 650 °C, to meet operational and efficiency goals for power production, with nitrate salts as one suggested heat transfer fluid. Unfortunately, much of the industrially available instrumentation for flow and pressure measurement is not rated for use above 450–500 °C.

The temperature limitations on most flow devices can be attributed broadly to materials compatibility. The ideal flow measurement device would be corrosion resistant, have minimal or no moving parts to minimize failures at high temperatures, and could be scaled from an R&D prototype to an industrial-sized device.

Technology currently exists for flow detection of ionic liquids at moderate temperatures (420 °C). The innovative nature of this work will expand current technologies by developing a prototype that is capable of withstanding the extremely high temperatures (~700 °C) desired for continuous operation in molten nitrate salts, while producing reliable and repeatable measurements of important flow parameters.

Hydrological Characterization of Karst Phenomenon in a Semi-Arid Region using In-Situ Geophysical Technologies

157311

Year 2 of 3

Principal Investigator: K. S. Barnhart

Project Purpose:

We are pursuing a new geophysical method for characterizing the hydrodynamics of semi-arid karst. The dissolution of soluble bedrock (e.g., limestone) results in surface and subterranean channels, called karst, which comprises 7% to 10% of the dry earth's surface. Karst serves as a preferential conduit to focus surface and subsurface water but, because of irregular structure and nonlinear hydrodynamic behavior, is difficult to exploit as a water resource or to protect from pollution.

Municipal/agricultural/energy/carbon storage/waste projects are projected for location in semi-arid regions, where karst often exists but is essentially impossible to characterize using standard, "wet karst" methods. Hence, the scientific challenge is to develop new techniques to gather karst hydrological information in terrains where karst features are dry except during infrequent rain and runoff events.

Ground-based geophysical tools are typically chosen to locate karst structural features when water is limited or absent. Unfortunately, past field studies have met limited success because aforementioned subsurface heterogeneities confuse low-resolution data. Even when karstic conduits are located, the original questions, pertaining to conduit hydrological significance, are left unanswered.

We are customizing emerging in-situ geophysical monitoring technology to generate time-series data during sporadic rain events. Electrical and seismic sensors are being connected to wireless "nodes," which can be left in the field for many months. Embedded software will increase sampling frequency during periods of rainfall. Further, we will develop parallel inverse code to determine subsurface parameters from this unique time-series data. We hypothesize that this contrast between no-volume flow in karst passageways during dry periods and partial- or saturated-volume flow during a rain event is detectable by these wireless sensor network (WSN) geophysical nodes.

The national, economic and energy security of the US is reliant on locating and characterizing suitable locations for energy production and waste disposal. The DOE is committed to promoting "scientific and technological innovation in support of that mission." Karst is a common geological feature; in many places, pollutants from municipal and agricultural waste have reached crucial water supplies via karst. The DHS's interest in national security preparedness also depends on improved characterization methodologies for preventing contamination of karst recharge points. The EPA is similarly committed to the security of water systems. Hence, the development of methodologies to characterize semi-arid karst hydrology will benefit Sandia, DOE, and other federal agency missions in energy technologies, waste disposal, and climate security by helping to differentiate safe and secure regions from those at risk.

Surface Electrochemistry of Perovskite Fuel-Cell Cathodes Understood In-Operando

158702

Year 2 of 3

Principal Investigator: F. El Gabaly Marquez

Project Purpose:

Solid-oxide fuel cells (SOFC) are electrochemical devices that convert fuels into electricity at efficiencies greatly exceeding combustion-based technologies. Operated in reverse as solid oxide electrolyzer cell (SOEC), renewable electricity can be converted into carbon-neutral fuels by reduction of water or carbon dioxide. Thus, it is widely anticipated that fuel cells and electrolyzers will be used for storing and inter-converting energy at large scales. Key to improving SOFC technologies is eliminating the kinetic bottleneck of the oxygen reduction reaction (ORR), which occurs on the cathode. The chemical state of the cathode surface critically controls the rates of surface reactions and solid-state transport. Unfortunately, the surfaces of perovskite-structured oxides, the state-of-the-art cathode materials, are extremely complex. Thus, developing new approaches to determining the surface chemical states during actual operation is extremely desirable.

This project represents basic research inspired to understand an important longstanding energy issue, namely, how do SOFC cathodes function at an atomic level? The innovation that makes this approach unique is the performance of detailed, quantitative in situ measurements of the surface chemical state while the system is operating. We are using in situ electrochemical x-ray photoelectron spectroscopy (EC-XPS) under near-realistic operating conditions of high temperature, gas activity and in the presence of spatially dependent electric potentials to study the solid-gas interphase of state-of-the-art cathode materials over single-crystal yttria-stabilized zirconia (YSZ). We are learning new microscopic chemical information about the processes that limit the rates and efficiencies of electrochemical energy storage and conversion. Knowing the chemical states of the surface and of the bulk and the macroscopic response of the electrolyzers/fuel cell (e.g., the current vs. voltage behavior and the impedance spectroscopy) will provide new insights into the complex processes occurring at cathode surfaces. When continuum models analyze the combined information, knowledge about which microscopic processes control device performance will be obtained.

Advanced Materials for Next-Generation High-Efficiency Thermochemistry 158808

Year 1 of 2

Principal Investigator: J. E. Miller

Project Purpose:

The purpose of this project is to rapidly advance the field of thermochemistry to produce a material that is capable of yielding CO from CO₂ at a 12.5% reactor efficiency (an important milestone for solar fuel technology). As materials cannot be fully divorced from system, we will also define the next-generation heat engine in which this benchmark is achievable.

Until recently, very little effort—apart from basic thermodynamic analysis—was extended towards understanding the most fundamental part of a metal oxide thermochemical cycle—the reactive oxide itself. Without this knowledge, system design was hampered, but more importantly, advances in these crucial materials were rare and resulted more from intuition rather than detailed insight. As a result, there are currently only two basic families of potentially viable materials, each of which has challenges. Having recently applied a level of scientific rigor not previously seen to the study of thermochemical materials, we are now able to define a characteristic property space that high-performing materials will occupy, one that includes such considerations as geometry and characteristic dimensions for transport, reaction rates, thermodynamics, and physical properties such as melting point and sublimation pressure. We will apply this knowledge to achieve our goal.

Sandia is a recognized world leader in the rapidly evolving field of beneficial CO₂ utilization, in particular the solar thermal approach adopted here. Despite rapid progress, solar thermochemistry remains high risk; a factor of 10–20 improvement is needed for it to reach its full potential: >12.5% life-cycle sunlight-to-hydrocarbon efficiency (numerous steps beyond CO efficiency targeted herein). Realizing these advances and the promise for our nation requires a multidisciplinary effort and specialized expertise and equipment. That is, only a few organizations such as Sandia can muster a meaningful effort in this field and increase the science and technology to reduce the readiness risk to private enterprise.

Designing Greenhouse Gas Monitoring Systems and Reducing Their Uncertainties

158809

Year 1 of 3

Principal Investigator: R. Bambha

Project Purpose:

A global climate treaty will likely be based on greenhouse gas (GHG) inventories supplied by participating countries. The inventory-based approach, which assigns emissions on the basis of economic and socioeconomic factors, is fraught with unacceptably large uncertainties in anthropogenic emissions. An approach based on atmospheric measurements will be critical for compliance verification on countrywide or regional scales. Furthermore, US compliance with a climate treaty will require implementation of effective policies at city, state, and regional levels. To evaluate policy effectiveness, state and municipal decision makers will need estimates of GHG emissions based on emissions sectors, such as transportation, power generation, and biomass burning. Existing attribution methods are inadequate for either treaty verification or policy evaluation, largely because they focus nearly exclusively on measurements of the most abundant GHG, CO₂, which has an enormous variable natural background. Inversion of CO₂ concentration measurements to source locations provides no information on source types, and current measurement databases used for these inversions lack the necessary spatial and temporal coverage.

The purpose of this project is to design a new measurement and analysis system for GHG source attribution suitable for treaty verification and regional or municipal policy evaluation. Our approach uses measurements of gases and particulates co-emitted with anthropogenic and biogenic GHGs, which serve as tracers of specific sources and can provide powerful information on source type and strength. This information is valuable for evaluating policy decisions and narrowing uncertainties on inversions for treaty verification, but the multidimensional nature of the associated inversion renders it intractable without co-design of the models and measurements to systematically constrain the problem. The unique approach and computational difficulty makes the project high risk. We are leveraging Sandia's unique GHG mobile laboratory to provide an attribution measurement testbed. Sandia's numerical simulation and analysis capabilities will be tightly coupled to support experiment design, characterize uncertainties, design sensor networks, and infer sources.

The Science of Battery Degradation

158810

Year 1 of 3

Principal Investigator: J. P. Sullivan

Project Purpose:

DOE has identified the transformation of our nation's energy systems towards clean energy technologies as its first mission statement goal. Electrical energy storage in the form of batteries is a key component of this vision. However, current large-scale battery technologies need substantial improvements in capacity and lifetime in order to meet performance and reliability goals. Although there has been considerable work to develop new battery materials, research to understand the limits of battery lifetime has lagged. The objective of this project is to identify, at the atomic level, the leading mechanism(s) that give rise to battery degradation. Detailed mechanistic understanding will be provided by a combination of newly developed and sophisticated characterization methods and atomistic to continuum-level modeling. Specifically, we are developing and applying in situ characterization methods that are based on transmission electron microscopy (TEM), scanning transmission x-ray microscopy (STXM), and high surface sensitivity optical spectroscopies to realistic full-scale lithium-ion battery electrodes and isolated battery particles. We are also developing new electrochemical approaches, including quantitative nanoscale electrochemistry and electrochemical entropy measurements as a function of cycling. Modeling methods include ab initio modeling of electrolyte decomposition at electrode surfaces and continuum-level modeling of electrochemical battery degradation signatures, including electrochemical entropy measurements. These methods and models are being used to evaluate leading proposed mechanisms of degradation, including electrolyte decomposition, which leads to solid-electrolyte interphase formation and growth, and mechanical fracture, cracking, and delamination within the solid electrodes. Importantly, we will compare our identified features of degradation generated through lab and computational studies to the features found in state-of-the-art high-lifetime commercial cells that have been cycled to the point of degradation. At the conclusion of this project, we expect to have a detailed understanding of the primary battery degradation mechanisms that will lead to new approaches to achieving high lifetime large-scale batteries.

Optimization of Distributed Waste Water/Water Reuse Systems 158811

Year 1 of 2

Principal Investigator: V. C. Tidwell

Project Purpose:

In much of the semiarid Southwest, regional water sustainability (supply meeting demand) is assured only when water reuse is included as an available water resource. In such cases, integrated planning of water and wastewater infrastructures can lead to economic efficiency and increased system sustainability. For example, integrated planning can address the degree to which new wastewater treatment facilities should be spatially dispersed, particularly in rapidly growing urban areas, in order to reduce conveyance and associated energy costs for the collection of wastewater and redistribution of reclaimed water. Uncertainties in future demand and water availability add complexity to the problem.

In a joint effort with the University of Arizona, decision support tools required for integrated water planning are being developed. This effort will build on those of a project “Optimization of Conjunctive Water Supply and Reuse Systems with Distributed Treatment for High-Growth, Water-Scarce Regions,” formerly supported by National Science Foundation’s Emerging Frontiers in Research and Innovation—Resilient and Sustainable Infrastructures (EFRI- RESIN) program. This project aims to use a triple bottom line (TBL—economic, social, and environmental costs/benefits) approach to evaluate water infrastructure alternatives under uncertainty. Integrating TBL objectives involves not only quantifying economic costs and associated uncertainty for wastewater reclamation infrastructure elements but also incorporating environmental impacts of reclamation activities through life cycle analysis and social/institutional constraints by scenario analysis. System optimization algorithms will be utilized to find solutions (including infrastructure location and sizing) that minimize TBL costs.

Water and wastewater systems have traditionally been considered as separate infrastructures, each subject to separate planning and operational approaches. Integrated planning achieves a more holistic view of the systems, and with it the potential for a greater degree of optimality in resource utilization. This type of approach is newer and has less-developed methodologies but could result in better infrastructure design for water and wastewater systems that considers the TBL.

Nuclear Fuel Cycle System Simulation Tool Based on High-Fidelity Component Modeling

158998

Year 2 of 3

Principal Investigator: D. Ames

Project Purpose:

DOE is currently directing extensive research into developing fuel cycle technologies that will enable the safe, secure, economic, and sustainable expansion of nuclear energy. The path to successfully develop and implement an advanced fuel cycle is highly dependent on the modeling capabilities and simulation tools available for performing useful relevant analysis to assist stakeholders in decision making. This project involves the development of a fuel cycle simulation tool that provides consistent and comprehensive evaluations of advanced fuel cycles, including uncertainty quantification and optimization. In addition, the ability to incorporate policy considerations, environmental impact, and economic projections are included. The resulting simulator has the unique features of being high fidelity in nature and capable of performing uncertainty analysis and optimization.

Current DOE fuel cycle simulation tools are large-scale system dynamics models that track material flow throughout the fuel cycle at the isotopic level and include decision-making capabilities. The design and nature of these code systems limit the level of detail achievable for reactor simulation and restrict their use for uncertainty analysis applications. Therefore, there is a need to provide a greater level of detail (high-fidelity) component modeling and the capability to perform uncertainty quantification. Such a tool could be used standalone or in conjunction with current fuel cycle analysis tools to provide a complete set of fuel cycle evaluation data to guide decision makers.

The project fills a gap in the performance of current fuel cycle simulation tools by incorporating whole-core 3D exact geometry reactor physics models that account for specific reactor designs, variations in design parameters, and quantifying the impact on the overall fuel cycle system. A new method and analysis approach has been developed and is being implemented to overcome limitations imposed by computational cost, which significantly restrict the ability to perform complete analysis of the system, particularly uncertainty quantification and optimization.

Development of a System Model for a Small Modular Reactor Operating with a S-CO₂ Cycle on a DoD Installation that Utilizes a Smart/Micro-Grid

158999

Year 2 of 3

Principal Investigator: T. G. Lewis

Project Purpose:

We have made significant progress on developing a system model capable of simulating the impact of a load varying smart/microgrid on a small modular reactor (SMR) and vice-versa for military installations. Results of this system model will benefit the selection of SMRs and smart/microgrid technologies. The military is actively seeking technologies capable of delivering energy security. The current model has been primarily focused on the nuclear power plant; light water reactors (LWR), sodium-cooled fast reactors (SFR), and high temperature gas reactors (HGTR) have been modeled. Current work will be focused on the microgrid technology aspect of this integrated energy system.

The application of a dedicated nuclear power system on a DoD installation has been proposed by those who are either in charge of DoD energy security and those who are proponents of nuclear energy, but neither party has investigated how to couple the requirements of the DoD and the rigidity of nuclear power systems operation constraints. Additionally, there is a focus on using advanced reactors due to their operations benefits and advanced power conversions systems, but neither technology has been rigorously investigated in terms of applicability to DoD facilities and microgrids. We propose to use a systems engineering approach focused on designing a model that is robust in scope to allow for temporal changes to a microgrid behavior while maintaining a high fidelity with respect to a nuclear reactor's behavior. Such a model will produce a system that best fits the unique needs and challenges for a DoD nuclear powered installation. This type of model can be coupled to experimental power systems and computational reactor models. The combination of synthetic grid disruptions and usage patterns will further increase the significance of system performance.

Toward a Predictive Understanding of Low Emission Fuel-Flexible Distributed Energy Turbine Systems

159259

Year 1 of 3

Principal Investigator: J. Oefelein

Project Purpose:

Using hydrogen derived from coal in power generation is one of the strategies being considered for eliminating CO₂ emissions from combustion. In a two-stage gas combustor, injection of hydrogen into a secondary combustor provides an effective means for achieving a wide range of power settings. However, when additional hydrogen is injected into the exit stream of the first stage turbine, the mixture may autoignite. This uncontrolled autoignition event is undesirable as it leads to strong acoustic waves and high levels of nitrogen oxides. Since hydrogen was not a main fuel in the past, studies of hydrogen combustion under gas turbine environments have not been extensively carried out. Autoignition of hydrogen depends on pressure in a nonlinear fashion and is sensitive to the unique transport properties of the small hydrogen molecules, making prediction of autoignition very challenging. For both steady and transient flames, high-fidelity Large Eddy Simulation (LES) is essential for obtaining a fundamental understanding of flame stability mechanisms. As such, we are conducting an LES study, in collaboration with the University of California, Berkeley, to model and understand 1) key stability mechanism(s) related to flame propagation and autoignition, and 2) the effect of pressure on hydrogen combustion over the range of 1 to 20 bar.

For power-generating turbine systems, the complexity of turbulence-chemistry interactions in lifted turbulent jet flames is a key challenging issue in adopting hydrogen as a potential alternative fuel. The small size of hydrogen molecules as compared to traditional carbon-containing gaseous fuels presents engineering challenges. Hydrogen molecules have higher diffusivity than other molecules, so combustion simulations must properly account for the different transport properties. High-fidelity LES, coupled with innovative capabilities in treating differential diffusion with a proper subgrid-scale model, are critical in understanding the stability mechanism in lifted hydrogen jet flames. Development of accurate models for hydrogen diffusion will allow for accurate and efficient engineering calculations towards designing future low-carbon power systems, an important potential contributor to DOE's energy security mission.

Opportunities for Waste and Energy 159302

Year 1 of 2

Principal Investigator: J. Westbrook

Project Purpose:

Increasing concern regarding the cost, security, and environmental impacts of fossil fuel energy use is driving research and investment towards developing the most strategic methods of converting biomass resources into energy. Analyses to date have examined theoretical limitations of biomass-to-energy through resource availability assessments, but have not thoroughly challenged competing tradeoffs of conversion of biomass into liquid fuel versus electricity.

Existing studies have focused on energy crops and cellulosic residues for biomass-to-energy inputs; however, the conversion of these biomass resources is often less energetically efficient compared to fossil energy sources. Waste streams are beginning to be recognized as valuable biomass to energy resources. Municipal solid waste (MSW) is a low-cost waste resource with a well-defined supply infrastructure and does not compete for land area or food supply, making it a potentially attractive, renewable feedstock. We have created the Waste Biomass to Energy Pathway model (WBEM) using a system dynamics approach to analyze the impact of converting MSW biomass to either bioelectricity or liquid fuel. Ultimately, the WBEM will incorporate macroscale feedback from supply chain costs, energy sector impacts, and greenhouse gas (GHG) production within the competing pathways of MSW to: 1) landfill, 2) transportation fuel, and 3) electricity in two states with distinct electric mixes: California and Wisconsin.

DOE biomass-to-energy strategies focus on liquid fuel and electricity pathways separately, rather than their direct competition. Regional diversities in energy supplies, costs, and biomass resources suggest considering these pathways in competition. MSW-to-energy modeling remains in its infancy, providing Sandia an opportunity to scientifically lead within this field. The system dynamics methodology allows a quantitative exploration of tradeoffs between these pathways by considering dynamics and feedback across them over time. This capability will guide understanding of how waste-to-energy technologies could more strategically advance bioenergy in the US, and provide a flexible framework able to apply to waste streams beyond MSW.

Enhancing National Security to Rare Earth Element Shortages through Uncertainty Analysis

160400

Year 1 of 2

Principal Investigator: P. Sanyal

Project Purpose:

Globalization of supply chains increases vulnerabilities to strategic technologies, so this project will create a network flow model that will enable the analysis of how foreign-produced raw materials can impact national security supply chains. This conceptual model minimizes trade costs subject to demand and supply constraints. Costs included in the objective function formulation include export tariffs, transportation costs, and “security” costs. Security costs measure the cost of trade between two countries that have dissimilar political interests, but trade with each other due to the economic benefits. Application of the conceptual model provides understanding of rare earth elements (REE) trade patterns across a number of “what if” scenarios. In other words, questions such as the following will be answerable: how would trade patterns change and security risks decrease if Australia and the US opened new rare earths mines. The project acquired REE trade data and analyzed it to understand the evolving trade patterns between countries. The project has also evaluated model alternatives to the current gravity-modeling framework to determine the validity of different modeling paradigms for REE trade.

In addition, the project will examine the effects of both implicit and explicit trade costs of REEs to various countries using a stochastic frontier econometric model. The estimates from this model will determine how trade costs play a crucial role in determining the level of REE trade between countries.

The benefit of the project will be new modeling approaches that enable a more comprehensive analysis of impacts of foreign-produced raw materials on strategic supply chains and of the factors determining those impacts. Additionally, the test application of the modeling approach to REEs will provide valuable insight into a problem of national significance.

Theoretical Foundations for Measuring the Groundwater Age Distribution

161864

Year 1 of 3

Principal Investigator: W. P. Gardner

Project Purpose:

Groundwater flow rates have important implications for groundwater resources, contaminant migration, and the isolation of hazardous wastes; however, flow rates and residence times inferred from individual environmental tracers have significant uncertainties. This project is exploring the theoretical foundations for measuring the groundwater residence time distribution in complex 3D aquifer systems using a broad suite of environmental tracers and incorporating this information in numerical models of groundwater flow. “Apparent” groundwater ages derived from tracer concentrations have been compared to modeled groundwater mean age, dramatically reducing parameter estimation uncertainty. However, a groundwater sample is a collection of particles with a complex residence time distribution; thus, comparison of a single modeled and tracer inferred age is fraught with uncertainty. The purpose of this project is to simulate the concentrations of multiple environmental tracers and assess methods of interpreting the information from tracers and the formal reduction in uncertainty of subsurface parameter estimates using tracer information.

Current work in this area suffers from two limitations: 1) most efforts have been tied to a particular field location, limiting universal application and 2) actual concentrations of tracers are not simulated due to the computational expense, thus incorporating inherent error by comparing a single fluid residence time. In this project, methods to constrain the residence time distribution from the concentration of multiple tracers are being derived, tracer information will be incorporated into formal parameter estimation, and uncertainty analysis routines using synthetic data sets. Finally, these methods will be used with an existing data set from a regional flow system. By focusing first on theoretical, numerical experimentation with the extensive numerical power at Sandia, this project can resolve fundamental questions of how to best utilize tracer information, the data worth of different tracers, and the computational requirements. These fundamental insights can then be applied to field data in any setting.

Chloride-Insertion Electrodes for Rechargeable Aluminum Batteries

161866

Year 1 of 3

Principal Investigator: N. Hudak

Project Purpose:

Demand for rechargeable battery systems continues to increase with the emergence of electric vehicles and the introduction of stationary energy storage to the electrical grid. Rechargeable batteries based on aluminum are attractive alternatives to those based on conventional chemistries (e.g., lithium and zinc) because of the high theoretical energy density and low cost of aluminum. An emerging type of rechargeable aluminum battery is based on room-temperature ionic liquids containing aluminum chloride. Aluminum metal has been extensively studied in such solutions, forming the basis for the negative electrode in a rechargeable aluminum battery. The purpose of this project is to explore candidate materials for the positive electrode, which have been far less explored. For this purpose, we are evaluating conjugated polymers as reversible chloride-insertion electrodes in room-temperature ionic liquids. This represents a significant advance, as there has been limited investigation of positive electrode materials for nonaqueous, room-temperature aluminum batteries. This work addresses issues of energy reliability and security because of the need for new battery chemistries that are based on inexpensive, domestically produced materials. The electrode materials will be quantitatively evaluated using performance metrics that are relevant to rechargeable batteries for electric vehicles and/or stationary storage. Conjugated polymers are especially interesting for this purpose because they are inexpensive, electronically conductive, and synthesizable by chemical polymerization or electropolymerization. The use of conjugated polymers as chloride insertion electrodes in aluminum electrolytes has been demonstrated only a few times. There is very little understanding of the effects of polymerization conditions, molecular structure, and solution composition on capacity, energy density, and cycling in aluminum chloride solutions. During the first year of the project, we have demonstrated the electrochemical synthesis of polypyrrole, polythiophene, and other conjugated polymer films in chloroaluminate ionic liquids and confirmed their identity with analytical techniques. We have also begun to examine the electrochemical behavior of these films in aluminum-based ionic liquids.

Hybrid-Renewable Processes for Biofuels Production: Concentrated Solar Pyrolysis of Biomass Residues

161868

Year 1 of 3

Principal Investigator: A. George

Project Purpose:

The purpose of this project is to create a system by which we can understand fundamental pyrolysis and gasification behavior of biomass and biomass residues, when subjected to a solar flux, in the context of producing biofuels and power from solar processing of biomass. To this end we are designing a reactor that will enable the study of single particles of biomass, in terms of the gas, tar, char yields and the composition of pyrolysis oils, under different conditions of exposure to solar energy. Comparisons between solar pyrolysis versus the current state of the art pyrolysis systems will enable an evaluation of inherent advantages and disadvantages of solar pyrolysis/gasification with the view toward developing a program in reactor optimization. To enhance the environmental advantages of solar pyrolysis further, the other aspect of this study is a focus on the biomass itself. Here, the specific pyrolysis and gasification behavior of biomass residues themselves will be studied, in this instance, residues of lignin. We will study lignin pyrolysis behavior in the solar pyrolysis reactor and compare this to its behavior in other systems. Currently, most data in the literature is a function of reactor configuration, with different reactor systems giving very different data, and it is difficult to isolate the effects of reactor design from product yields, which therefore hampers optimization and scale-up efforts. Given that the solar reactor will be designed to study single particle behavior, this will enable the study of lignin pyrolysis behavior itself. Being able to process/upgrade lignin effectively to fuels/chemicals using pyrolysis is one of the key challenges in biorefinery economics, and any fundamental information on lignin behavior will have a significant impact on lignocellulosic biorefinery development.

Computational Optimization of Synthetic Water Channels

162035

Year 1 of 1

Principal Investigator: S. Rempe

Project Purpose:

Membranes for liquid/gas separations and ion transport are critical to water purification, osmotic energy generation, fuel cells, batteries, supercapacitors, and catalysis. Often these membranes lack pore uniformity and robustness under operating conditions, which can lead to a decrease in performance. The lack of uniformity means that many pores are non-functional. Traditional membranes overcome these limitations by using thick membrane materials that impede transport and selectivity, which results in decreased performance and increased operating costs. For example, limitations in membrane performance demand high-applied pressures to deionize water using reverse osmosis. In contrast, cellular membranes combine high flux and selective transport using membrane-bound protein channels operating at small pressure differences. Pore size and chemistry in the cellular channels is defined uniformly and with subnanometer precision through protein folding. The thickness of these cellular membranes is limited to that of the cellular membrane bilayer, about 4 nm thick, which enhances transport. Pores in the cellular membranes are robust under operating conditions in the body. Recent efforts to mimic cellular water channels for efficient water deionization produced a significant advance in membrane function. The novel biomimetic design achieved a 10-fold increase in membrane permeability to water flow compared to commercial membranes and still maintained high salt rejection. Nevertheless, it is not clear why the membrane performs so well. We will use high-performance computing to interrogate the structural and chemical environments experienced by water and electrolytes in the newly created biomimetic membranes. We expect that a comparison of solvation environments between the biomimetic and cellular water channels will inform efforts to optimize and tune the performance of synthetic biomimetic membranes for applications in water purification, energy, and catalysis.

Creativity derives from biomimicry to revolutionize membrane design, which has stagnated over the last three decades. Innovation comes from using molecular modeling, informed by experiment, to understand the design principles of cellular and synthetic membranes.

Summary of Accomplishments:

Following the R&D 100 award for development of biomimetic membranes (*R&D Magazine*, 2011), we applied atomistic simulation to probe the structural and chemical motifs that account for function in these membranes. We developed the first atomistic model of the biomimetic membranes by creating a computational procedure to mimic atomic layer deposition (ALD) of polymer into a nanopore formed of silica. The resulting structure provides the first observation of the atomic-scale organization of polymer after deposition, and reveals a dense and stable network organization.

We analyzed solvation free energies for transferring sodium (Na^+), chloride (Cl^-), and water molecules (H_2O) from bulk liquid water to the channel interior. We compared the computed solvation free energies to the same values computed for transfer into the cellular water channel, aquaporin, and to an unsupported polymer. The unsupported polymer was constructed to mimic a commercial membrane, which stands freely on a substrate, unconfined by nanopore walls.

The results indicate that the ALD membrane mimics the cellular water channel in that both provide environments that destabilize Na^+ and Cl^- ions. In contrast, the unsupported polymer provides an environment that stabilizes Cl^- ions. Water appears to be more favorably solvated in the cellular water

channel due to the formation of water chains, which do not occur in simulations of the biomimetic membrane nanopore.

These results suggest that the small ion conductance observed experimentally for the biomimetic membranes arises due to defects in the membrane, rather than due to a favorable ion solvation environment in the active region formed by ALD. Further, they suggest that enhanced water conductance may be attained by increasing the density of polar groups to stabilize neighboring waters. An environment that stabilizes neighboring waters would favor formation of chains of hydrogen-bonded waters chains, and thus water transport in collective groups rather than individually.

Significance:

The computational analysis of nanopore structures and function, both in synthetic and cellular membranes, advances our understanding of nanoscale mechanisms and informs efforts to design membranes for specific functions. Here, we targeted toward fast water flux and ion rejection for efficient water desalination by reverse osmosis technology. Nevertheless, the computational framework developed can be used to interrogate the relationships between structure and properties in any complex nanostructure. For example, we can use the computational tools to analyze and propose new designs for membranes used in water purification or osmotic energy generation by electrodialysis. Efficient separations technology promotes water security, an important initiative of DHS and of DOE in the context of energy security.

Refereed Communications:

D.M. Rogers, D. Jiao, L.R. Pratt, and S.B. Rempe, "Structural Models and Molecular Thermodynamics of Hydration of Ions and Small Molecules," *Annual Reports in Computational Chemistry*, vol. 8, pp. 71-127, 2012.

Integrating of SD and PRA to Create a Time-Dependent Prediction of the Risk Profile of a Nuclear Power Plant

162299

Year 1 of 3

Principal Investigator: M. R. Denman

Project Purpose:

The purpose of the project is to demonstrate the linking of aging, maintenance and operational models to quasi-static fault trees produced by reliability equations. This process will involve treating aging and component uncertainty in dynamical models as external inputs, parameter changes, or state changes. Ultimately, the coupling between Probabilistic Risk Assessment (PRA) and System Dynamics (SD) will both remove non-conservative approximations and improve stakeholder confidence in PRA.

PRA is the primary tool used to risk-inform nuclear power regulatory and licensing activities. Risk-informed regulations are intended to reduce inherent conservatism in regulatory metrics that are built into the regulatory framework by quantifying both the total risk profile as well as the change in the risk profile caused by an event or action.

SD has been used to understand unintended time-dependent feedbacks in both industrial and organizational settings. We propose that SD models can simulate changes to the reliability in Structures, Systems, and Components that can adjust the basic event probabilities at the base of a fault tree. Dynamic system models are being used to adjust the trees to explicitly incorporate aging effects and/or examine changes in system reliability during a maintenance event or accident. These tools can dramatically expand the applications of risk-informed decision making by adjusting risk metrics for evolving conditions in a structured manner.

Dynamic models can interface with the PRA through many different approaches. For this study, the focus will be to identify plausible behavior modes for systems undergoing maintenance and aging, along with dynamic events (e.g., startup, shutdown) that might benefit from analysis of reliability dynamics. In order to accomplish this goal, three different dynamic models are utilized:

1. Functional — How does the system work?
2. Aging and Maintenance — How does time affect component performance?
3. Operational — What decisions can the operator make given the information available?

Heavy Duty Vehicle and Infrastructure Futures 164667

Year 1 of 3

Principal Investigator: A. C. Askin

Project Purpose:

In the US, heavy-duty vehicle (HDV) fleets comprise a significant fraction of total fossil fuel consumption, which has profound implications for national security, environmental sustainability, and economic stability. Therefore, directing the future development of this sector toward reducing petroleum consumption while meeting the needs of fleet operators is critical to mitigating future consequences. New alternative fuel and power system technologies in varying stages of development and commercialization comprise a broad portfolio of options for new vehicle design and current vehicle modifications. The breadth of this portfolio necessitates a tool to evaluate the interdependency of the technical, economic, and stakeholder factors driving the evolution of heavy-duty vehicle resource consumption and emissions generation. Critical questions to be answered include: How are vehicle technology innovations best leveraged to address national security, environmental, and economic concerns? What are the capability gaps and major non-technical issues impeding industry transformation? What attractive fueling infrastructure options are available to take advantage of HDV transit patterns and fleet scales? A Heavy-Duty Vehicle Pathways Model (HDVPM) will be constructed to address these questions.

Although some modeling efforts have begun to illuminate the complexities of transforming the HDV sector, a comprehensive model accounting for the breadth of vehicle inventory, the impact of potentially transformational technologies, and the necessary infrastructure development remains missing. This project will construct a capability for evaluating the HDV fleet energy efficiency outlook based on supply-demand interactions between fuel and infrastructure availability, technology readiness, and primary energy sourcing. The model will incorporate the potential for both technical leaps and impediments throughout the diverse HDV fleet, culminating in the ability to assess technology development portfolios and identify critical decision points for sector transformation. Developing the model will create the capacity for identifying and understanding the principal mechanisms driving the trajectory of the HDV industry with regard to resource consumption and environmental sustainability.

Nanoscale Piezoelectric Effect–Induced Surface Electrochemical Catalysis in Aqueous Environments

165464

Year 1 of 3

Principal Investigator: H. Liu

Project Purpose:

We propose advancing the knowledge of the piezoelectric-induced surface catalysis in ferroelectric nanostructures. Ferroelectrics are “smart” functional materials whose physical properties are sensitive to changes in external conditions such as electric field, pressure, and temperature. Although ferroelectrics are widely used in sensors and microelectromechanical systems (MEMS), activating and catalyzing surface electrochemical reactions via the surface charges generated by piezoelectricity is poorly understood. We anticipate that advancing the scientific understanding of the reactivity of nanoscale ferroelectrics in fluidic environments will open a broad range of new applications for ferroelectric material-based surface catalysis and aqueous sensing, establishing a differentiating leading-edge capability relevant for addressing future mission needs.

As an initial demonstration, we propose investigating industrially scalable electrospun ferroelectric nanofibers as a novel membrane component for mitigating membrane biofouling in water treatment (a major obstacle that decreases membrane life and prompts excessive back-washing). Embedded ferroelectric nanofibers in filtration membranes have the potential to electrochemically decompose organic matter in situ on the membrane surfaces, thereby mitigating membrane biofouling.

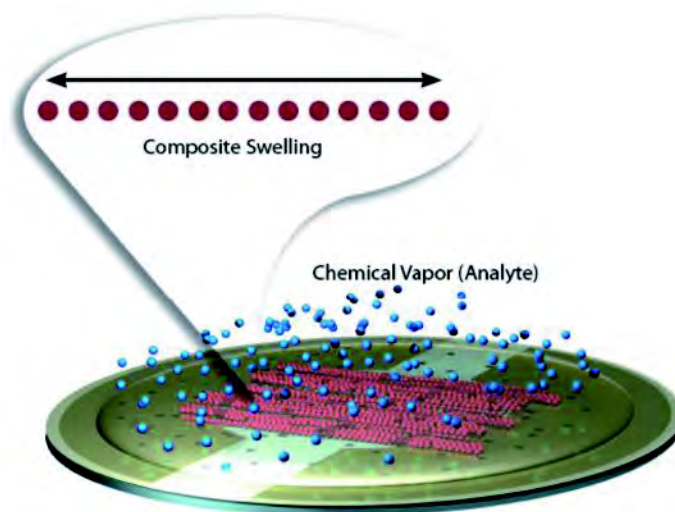
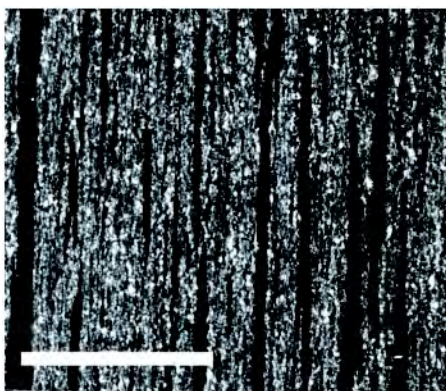
We investigated reactivity of mechanically excited ferroelectric nanofibers in fluidic environments to identify the microscopic mechanism of effective piezoelectric effect and electrochemical reaction coupling. Electrospun nanofibers will be used because they have particularly large reactive surface areas. Nanofiber geometry can also potentially enhance the piezoelectric responses due to intensified piezoelectricity ascribed to the flexoelectric effect on the nanoscale, and nanofibers possess high sensitivity to small forces. With fabrication and materials engineering through electrospinning and sol-gel techniques, systematic studies of electrospun ferroelectric nanofibers will offer optimum size and material selection as an excellent platform to study nanoscale piezoelectricity-induced electrochemical reactivity on ferroelectric surfaces in solutions.

INTERNATIONAL, HOMELAND, AND NUCLEAR SECURITY INVESTMENT AREA

This investment area funds research into a variety of efforts designed to mitigate the risk posed by chemical, biological, radiologic, and nuclear threats against domestic, international, and military populations, as well as threats posed by nuclear and biological proliferation. Through the effective use of science, technology, and full-spectrum system solutions, projects are aimed at providing integrated and sustainable solutions to high-consequence threats, through system design, technology development, and deployment across the threat spectrum — from anticipate to prevent, identify, respond, and recover. By leveraging Sandia's technologies, engineering, and systems integration competencies to engage in global nuclear risk reduction, the investment area seeks to foster interagency and international partnerships in nuclear security, nonproliferation and arms control. Aviation and border security and the ST&E necessary to support these initiatives also fall within the purview of this investment area.

Development of Chemiresponsive Sensors for Detection of Common Homemade Explosives Project 149568

Readily made from common household automotive items such as hair bleach and battery acid, homemade explosives (HMEs) present an emerging threat to both US military forces and civilians. In the Middle East, where the supply of munitions from previous conflicts has more-or-less dried up, terrorists are progressively turning their attention toward improvised explosive devices (IEDs) with an energetic-material component derived from commonly available household agents, most notably hair bleach, fingernail polish, and automotive battery acids. Exemplary is triacetone triperoxide, a dangerously unstable homemade explosive that was used as an explosive initiator by British shoe-bomber Richard Reid, and whose synthesis requires the reaction of H_2O_2 (hydrogen peroxide) with acetone in a sulfuric acid medium. More importantly, there is no currently field-deployed technology to detect such HMEs, and therefore, this project's work with portable sensors — polymer-based devices known as field-structured chemiresistors (FSCRs) — is directly aligned with Sandia's national security mission in threat detection. FSCR research examines several schemes for field-detection of the presence of H_2O_2 , which could, in turn, alert security personnel to the potential presence of an HME.



Polymeric matrix (micrograph, left, bar = 3 mm) and schematic drawing during swelling upon binding analyte (right), that could serve as chemiresistor detectors of homemade explosives. Upon binding a relevant analyte the polymer swells with a separation of its components and an increase in its resistivity.

Development of a Sustainable Anthrax Diagnostic Test for Countering the Biological Threat

Project 158813

Perhaps no biothreat organism has received as much publicity as *Bacillus anthracis*, the causative agent in anthrax. And while the toxic proteins synthesized and secreted by this bacterium are well-known and well-studied, the organism's worldwide ubiquity makes detection of highly pathogenic strains of primary importance to both biothreat mitigation and public health. Hence, this current project stands out as both biothreat mitigator and public health initiative. In this instance, the project has assembled a team of microfluidic/microsystem engineers, molecular biologists, and a project lead with a deep understanding of the issues entailed with trying to accurately test for *B. anthracis* in a third-world context.

The answer, other than training, is to make detection simple, requiring minimal sterile laboratory culturing technique and providing a strong, unambiguous colorimetric test for the bacteria. Such is the nature of this multifaceted project. The major thrust is to develop an inexpensive credit-card-sized chip requiring no power or other instrumentation, operable by individuals with minimal training, and self-sterilizing after a diagnostic assay for anthrax (or other organism) has been completed. The one opening in the chip, for inoculation, closes after that step rendering the device into a closed system. The channel-free fluidics device mixes a sample inoculum with a tiny amount (0.3 mL) of culture medium, and after 24-hours of growth in the sealed microchamber, exposes that culture to a test chamber that changes color in the presence of anthrax and its toxic proteins. A magnetically controlled valve closes the growth chamber and opens the test chamber.

The fluid moves between chambers at different depths in the device by simple shaking or tapping the device. The final step after reading the test result is to transfer the sample to a chamber pre-loaded with bleach to destroy any contained organisms. There is no exit port.

The project includes design of a better, more easily read test that does not rely on the more-expensive commercial test strips, which the project prototype is currently employing. The approach is to utilize conjugated-antibodies whose variable "business end" specifically bind to and identify *B. anthracis*' toxic proteins. One approach is to conjugate the antibodies at their Fc or constant end with gold nanoparticles, which when brought close together exhibit a red-to-blue colorimetric shift. A second, possibly more highly visible method is to substitute cadmium-selenium core-shell quantum dots, which upon excitation emit visible light. The wavelength of the emission can be tailored by varying the size of the quantum dot core and the emission would improve the target detection limit by several orders of magnitude.



The anthrax detection chip, current iteration with commercial test strip.

International, Homeland, and Nuclear Security Investment Area

Development of Coherent Germanium Neutrino Technology (CoGeNT) for Reactor Safeguards 141616

Year 3 of 3

Principal Investigator: B. Cabrera-Palmer

Project Purpose:

Antineutrinos are extremely penetrating elementary particles that have unique features of interest for safeguards at nuclear reactors: they cannot be shielded, are inextricably linked with the fission process, and provide direct real-time measurements of the operational status, power and fissile content of reactor cores using equipment that is independent of reactor operation. Based largely on work performed by Sandia and Lawrence Livermore National Laboratory, the International Atomic Energy Agency (IAEA) Novel Technologies Division has identified antineutrino detection as an important operation.

We propose a new antineutrino detector that is much smaller and safer and, therefore, more likely to find widespread acceptance as a monitoring tool. This novel detector would be based on high-purity germanium (HPGe) detector technology, which has been widely used for gamma-ray spectroscopy (including by the nuclear power industry). Our goal has been to create a new type of electronic readout system for an HPGe detector that will enable us to be sensitive to an as-yet undetected antineutrino signature — the coherent neutrino-nucleus scattering. This process is universally predicted and has a much higher probability of interaction such that a germanium detector of 10 kg would have similar sensitivity to 1 ton of the current scintillator based detection technology. This should allow a significant reduction in the necessary scale for a complete detector system and more flexibility in finding locations suitable for detector installation. If successful, the Coherent Germanium Neutrino Technology (CoGeNT) could yield higher sensitivity to reactor fuel composition variation.

Summary of Accomplishments:

The noise analysis of the analog electronics led us to conclude that the preamplifier and high-voltage circuits of the CANBERRA (CANBERRA Corp., Meriden, CT) broad energy germanium (BEGe) detector were already optimal, and so, no modification of the circuitry beyond the junction field effect transistor (JFET) amplification stage should significantly improve its noise performance. Testing the BEGe detector element with the Lawrence Berkeley National Laboratory's front-end and electronics strongly suggested that the main noise component (1/f noise) is mainly capacity dependent, and the BEGe's noise performance was limited by its own capacitance. We proceeded to fabricate a new P-type Point Contact (PPC) detector element with a 1-mm point contact and thus, with lower capacitance, expecting a significant reduction from the 4-mm diameter of the BEGe. Fabrication and assembly of a new PPC and the corresponding mechanical mounting and electrical components have presented issues inherent to the process of creating a novel system with stringent performance constraints. These difficulties have prevented us from achieving a full noise optimization within this project's timeframe.

Our analysis of the background rates obtained in other deployments validates the intended shielding design. Neutrons require special attention due to the nature of their background signal, and, thus, an anticoincidence internal veto made of plastic organic scintillator was the only shielding component that we decided was worth testing within this project. The anticoincidence veto showed very good light collection uniformity and energy resolution. The resultant hardware threshold with four photomultiplier

tubes (PMTs) is 100 keVee. One way to decrease the threshold is by increasing the photocathode coverage by adding more PMTs, but the increase in internal radioactivity must then be considered.

Significance:

Our results significantly advanced the understanding of the limiting factors in creating a very-low noise HPGe system that would be sensitive to antineutrino detection. Though we did not achieve our goal of testing and stably operating a low-noise system, we were able to isolate the main physical parameters causing the current noise performance and began preliminary testing of a new system. As other antineutrino detector designs, our foreseen system would allow to directly monitor the operation of a nuclear power reactor, non-intrusively and in real-time, but it would be a safer and smaller alternative. This outcome aligns with DOE's mission in low-carbon energy sources.

Graded Engagement of Small Aircraft and UAVs for Physical Protection 141678

Year 3 of 3

Principal Investigator: R. L. Burchard

Project Purpose:

General aviation aircraft have been used throughout the history of flight for assaults on ground-based assets, from Kamikaze attacks in World War II to the use of civilian aircraft for terrorist attacks on the World Trade Center. A large number of civilian and military assets are vulnerable to threats posed by low-flying aircraft such as small fixed wing airplanes, helicopters, and unmanned aerial vehicles possibly carrying hazardous or explosive payloads. To counter these aerial attacks, a system is needed that is able to detect a possible threat, assess its potential risk, discourage the aircraft from proceeding toward the target, and if necessary prevent the craft from carrying out a nefarious task.

Several systems currently exist for the detection, tracking, warning, and destruction of threatening aircraft. However, most of these systems use lethal measures to prevent the aircraft from reaching its intended target. Since many small aircraft mistakenly enter restricted airspace due to communication or navigation errors, new approaches are needed to remove unauthorized aircraft from restricted airspace without using lethal force. One possible approach is to use “graded engagement” as a means to prevent small aircraft from proceeding on unauthorized flight paths.

The graded engagement concept applies increasing levels of force to alter the unauthorized aircraft’s flight path. However, detection and warning systems that employ graded engagement do not currently exist. For a graded engagement approach to be realized, several technological gaps must be addressed.

Summary of Accomplishments:

The Improvised Air Attack Defense (IAAD) project worked to identify techniques and technologies that could help prevent improvised aerial attacks from small, general-aviation aircraft. The project assessed a wide range of current technologies to determine the merit of employing graded engagement as a method to mitigate risk from airborne attacks to civilian and military targets. Less-than-lethal and speculative technologies were evaluated for their ability to detect potential aerial threats and establish communications with pilots flying threatening aircraft.

The IAAD project developed and modeled a graded engagement strategy to minimize the threat of small, general-aviation aircraft from flying through restricted airspace. The work also identified a set of tools and technologies necessary to develop a fully integrated situational awareness system.

The research identified and developed technologies for employing graded engagement strategies to help reduce air threats. Through this research two new technology concepts were developed:

1. Hail All Frequencies — a communication method to simultaneously broadcast warning messages to pilots on all channels of the very high frequency (VHF) aviation band
2. Moving Footprint — a dynamic situational awareness application that graphically depicts an aircraft of concern’s reachable flight area in a given time period

Significance:

This research demonstrated that aerial attacks can be minimized by employing graded-engagement strategies to reduce the number of aircraft entering restricted airspace. The work demonstrated that early threat detection and situational awareness can aid the deterrence of future attacks. Deploying these new

technologies near major assets would provide increased situational awareness by defining the threat timeline and help the command authority make better-informed decisions regarding threats to the nation's airspace. This work will, therefore, benefit DoD and DHS in their homeland protection activities.

Rapid Radiation Biodosimetry to Mitigate Exposure Scenarios 141680

Year 3 of 3

Principal Investigator: G. J. Sommer

Project Purpose:

Radiological and nuclear incidents raise significant health concerns. Sandia systems analyses addressing high-consequence events highlight the need for rapid triage and assessment of priority victims and the “worried well” following a radiological event. Responsive therapeutic administration requires dosimetry tools that detect doses of 1-8 Gy (1 Gray [Gy] = 1 Joule of radiation absorbed per kg tissue) within 24 hours post-exposure for avoidance of long-term health effects and improved survival rates. For mass-exposure scenarios, these tools must be available at the point-of-incident and operate at a high rate. However, state-of-the-art biodosimetry fails to meet these requirements. Current early response measures (i.e., time-to-onset of vomiting and external emission dosimetry) provide only broad qualitative dose approximations, lacking the sensitivity required for proper therapeutic response.

The Armed Forces Radiobiology Research Institute (AFRRI) has identified changing protein and leukocyte levels in blood within minutes to days following exposure to even low levels of radiation through exhaustive animal model testing. However, traditional methods for detecting these biomarker fluctuations do not satisfy logistical needs of DHS scenarios. In this work, we are addressing this unmet need by: 1) using Sandia’s proven centrifugal microfluidic platform to detect biomarkers for radiation biodosimetry by testing animal model samples in collaboration with the AFRRI and 2) demonstrating that the portable platform satisfies the need for a rapid, deployable biodosimeter enabling timely and effective therapeutic response even for large population exposure incidents. This project expands Sandia’s biodefense diagnostics capabilities into the Rad/Nuc detection mission space, a previously unexplored area for Sandia.

Summary of Accomplishments:

We have developed a novel centrifugal, “lab-on-a-disk,” microfluidic platform for point-of-care diagnostic applications: SpinDx. Using this platform, we have designed assay architectures, which allow simultaneous detection/quantification of protein and cellular biomarkers from a small volume of whole blood — an important achievement for point-of-care diagnostics. Notable technical accomplishments include improving our detection limits to ultrasensitive levels (~100-fold more sensitive than gold-standard ELISA [enzyme-linked immunosorbent assay]). Bioconjugate chemistry for reagent creation has been optimized, enabling assay testing for new targets with less than one-day turnaround and minimal lot-to-lot variation. Calibration curves for 8 AFRRI radiation-responsive protein markers with dynamic ranges bracketing the clinically relevant concentrations in whole blood have been generated. We have also developed novel on-disk routing methods; a single sample can be loaded into an inlet port, and then routed to individual channels for processing. Further, we have improved our fabrication methods such that large batches of disks can be produced in high throughput with minimal effort by using injection-molding procedures. We have also improved our platform instrumentation such that all disk spinning and analysis steps are pre-programmed and automated. Our custom LED-based fluorescence detector is mounted on linear stages enabling rapid scanning of the channels for automated results output. We have implemented a high-speed industrial camera and strobe to capture on-disk transport and mechanics in real-time while spinning. We have developed the first one-step assay for quantification of circulating cell-free DNA assay — an important biomarker indicative of cellular necrosis. Finally, we have validated our platform in collaboration with AFRRI with a blinded total-body irradiation mouse model study. Our platform performed very well, achieving

high levels of sensitivity and specificity utilizing the unique multiparameter dose discrimination enabled by SpinDx.

Significance:

This research fills an unmet need in deployable diagnostics for radiation biodosimetry; thus, this work directly impacts national security and the mission of DHS by enabling vastly improved and informed medical intervention in scenarios of mass radiation exposure, such as deployment of a radiological dispersal device (RDD) and urban nuclear terrorism. This research will provide new approaches for exposed population triage and assurance of the worried well during such events.

Remote Sensing using Optical Filaments

141931

Year 3 of 3

Principal Investigator: M. Pack

Project Purpose:

Ultrashort laser pulses have demonstrated an intriguing array of possibilities for open air remote sensing due to the ability to form optical filaments. An optical filament forms when the peak power of a laser pulse exceeds the critical power for self-focusing. In this case, the laser pulse begins to spatially collapse (i.e., focus) until this collapse is arrested by the formation of a plasma which creates a negative lens. The beam diameter stabilizes at about 100 microns and the pulse propagates over long distances (up to several kilometers) with a constant beam diameter of 100 microns.

Optical filaments have many advantageous characteristics for remote sensing. For example, the trailing edge of an optical filament generates a white-light super continuum with preferential scattering in the backwards direction. This white-light source has been used in Lidar systems for broadband absorption spectroscopy with impressive results.

We are investigating the application of femtosecond laser pulses and filamentation to the study of remote sensing in liquids.

The work is a collaboration with Texas A&M University.

Summary of Accomplishments:

This year, we observed a host of previously undocumented phenomena involving intense femtosecond laser pulses at an air-water interface. These phenomena are related to the birefringence induced by high peak intensity femtosecond laser pulses. We also demonstrated the application of laser filaments in water to achieve subdiffraction limit resolution imaging. Finally, we explored the dynamics of energy transfer between laser filaments in liquid methanol.

Significance:

Our work explores fundamental physics related to remote sensing. While the research has broad applications to remote sensing, the fundamental nature of our research results in a long time horizon for potential applications (possibly five years or longer). Optical filamentation in liquids, especially water, offers the possibility for filament-induced breakdown spectroscopy to characterize the chemical composition of oceanic surface waters. Additionally, nonlinear propagation through water of femtosecond laser pulses has interesting implications for communications and remote sensing that are still being investigated.

Refereed Communications:

M. Zhi, K. Wang, X. Hua, B.D. Strycker, and A.V. Sokolov, "Shaper-Assisted Phase Optimization of a Broad 'Holey' Spectrum," *Optical Express*, vol. 19, pp. 23400-23407, November 2011.

K. Wang, B.D. Strycker, D.V. Voronine, P.K. Jha, M.O. Scully, R.E. Meyers, P. Hemmer, and A.V. Sokolov, "Remote Sub-Diffraction Imaging with Femtosecond Laser Filaments," *Optics Letters*, vol. 37, pp. 1343-1345, 2012.

B.D. Strycker, M. Springer, C. Trendafilova, X. Hua, M. Zhi, A.A. Kolomenskii, H. Schroeder, J. Strohaber, H.A. Schuessler, G.W. Kattawar, and A.V. Sokolov, "Energy Transfer between Laser Filaments in Liquid Methanol," *Optics Letters*, vol. 37, pp. 16-18, 2012.

Modeling and Simulation of Explosive Dispersal of Liquids 141932

Year 3 of 3

Principal Investigator: A. Brown

Project Purpose:

Explosive dispersal of liquids is a problem of great interest to this nation. It is important to be able to predict the resulting extent, timescale, and pattern of dispersal. In these scenarios, the liquid is initially propelled outward, either as liquid sheets through cracks that have been initiated in the container, or as an outward propagating liquid shell if the container is entirely fragmented, or a combination of the two. The outward expansion of the product of initial detonation rapidly accelerates these liquid sheets. A complex sequence of Rayleigh-Taylor, Richtmyer-Meshov, and other secondary instability mechanisms follow that shred the liquid jets and sheets into a dispersion of tiny droplets. The problem of liquid dispersal can thus be separated into a near-field and a far-field regime, where the initial ejection of the liquid and its evolution to a fine mist of droplets will be termed near-field. The subsequent evolution of the droplets and their interaction with the ambient air and the detonation products will be termed far-field. In collaboration with the University of Florida, we have pursued detailed hydrodynamic modeling and simulation of the initial ejection of the liquid, its subsequent break-up process and the final far-field dispersion of the liquid droplets. A combination of stability analysis, population balance, and large-scale scientific simulations has been used to address this problem.

Summary of Accomplishments:

This project led to the numerical evaluation of detonation shock wave growth of instabilities. Viscous and inviscid cases were evaluated. In the case of viscous problems, the peak instability growth is found to be related to the Reynolds number, and there was found to exist a critical wave number away from which the growth of instabilities decreases. The models were also evaluated with solid particles in the gas region.

Significance:

The models and methods developed in this study relate to shock physics, an integral part of Sandia's mission. The models developed and analyzed help to interpret the behavior of detonating systems, which provides tools for counterintelligence, detonating systems in alignment with DoD missions.

Refereed Communications:

M.R. Mankbadi and S. Balachandar, "Compressible Inviscid Instability of Rapidly Expanding Spherical Material Interfaces," *Physics of Fluids*, vol. 24, p. 034106, 2012.

Power Reduction Techniques for Modern Modulation Schemes 142044

Year 3 of 3

Principal Investigator: R. J. Punnoose

Project Purpose:

Wireless communications provides a richly challenging setting for many signal-processing applications. The work proposed focuses on addressing some challenges in spectrum and power efficiency for wireless communication systems. Specifically, a convex programming-based power saving technique for orthogonal frequency domain multiplexing (OFDM) signals has been developed that requires no bandwidth overhead and reduces the peak-to-average power (PAPR) at the transmitter, thereby allowing power amplifiers to be operated at more efficient operating points. This method extends to multi-antenna, multiple input, multiple output (MIMO)-OFDM systems, and also multi-user OFDMA systems with attractive distributed and low-complexity implementations. Simulating these methods in software and measuring their performance will be considered. A secondary focus of this work will be signal detection and estimation under noisy conditions. The goal of this signal processing can be, for example, to mitigate interference from multiple friendly sensors operating in the same bandwidth (for spectral efficiency reasons) or identifying and trying to recover from unfriendly jamming efforts. Methods from previous works on blind signal separation will be extended and specialized to the domain of telemetry systems. Specific attention will be given to jamming detection and mitigation. We hope advances in these areas lead to more efficient and robust wireless communication solutions.

Summary of Accomplishments:

The research has yielded results in two areas of study. The first is in the reduction of peak-to-average power ratio (PAPR) in OFDM and linearly precoded systems. This includes multi-user systems using OFDMA or single carrier (SC)-FDMA as well as MIMO systems using space-time block-codes (STBC)-OFDM. The second is in blind signal separation. The particular problem studied was an example from bioinformatics; however, the mathematical techniques are applicable to more general signal processing problems as well.

The first publication for the PAPR reduction work, “A Convex Optimization Approach to Reducing Peak-to Average-Power Ratio in OFDM”, covers a formulation of the tone injection method for PAPR reduction in OFDM and a proposed semi-definite programming (SDP) solution. Although that solution performs well in terms of PAPR reduction and/or bit error rate (BER) reduction, it is computationally expensive. Subsequent investigations yielded a linear programming approach that trades off some PAPR reduction performance for computational complexity. It has also been shown that this PAPR reduction scheme can be applied to any generic linearly precoded transmission, of which OFDM and its variants are only special cases.

Blind signal separation was studied in the context of a linear mixing network. The objective was to recover a number of source signals from a set of noisy mixtures (i.e., linear combinations) of the source signals. In the problem under study, the mixing matrix was assumed to have zeros at known locations and to satisfy certain identifiability conditions known as the network component analysis conditions. Mathematical techniques based on signal subspace theory were developed to recover the source signals and were demonstrated to have superior performance when compared to conventional techniques such as principal component analysis (PCA), independent component analysis (ICA), and Bayesian Decomposition (BD).

Significance:

This work in power-efficient wireless communication may be applied in many areas where available energy for communication is restricted. Some relevant areas are JTA telemetry (DOE), long-term sensor data acquisition (DHS), and covert communication (DoD).

Refereed Communications:

N. Jacklin, Z. Ding, W. Chen, and C. Chang, "Noniterative Convex Optimization Methods for Network Component Analysis," *IEEE/ACM Transactions on Computational Biology and Bioinformatics*, vol. 9, pp. 1472-1481, September 2012.

Modeling a Chemical Defense Strategy 148373

Year 3 of 3

Principal Investigator: T. H. Miller

Project Purpose:

Despite the long history of use of chemical weapons and repeated indications that terrorist groups possess both the ability and intent to employ chemical agents, surprising little attention has been focused on developing defensive concepts, much less a comprehensive strategy for civilian chemical defense. The objective of this project will be to develop a comprehensive model of chemical terrorism events to enable the clear delineation of which phases of the attack cycle provide optimal opportunities for intervention, what strategies offer the most promise of preventing or mitigating these attacks, and where significant gaps exist in our capabilities to prevent, detect, or respond to a potential attack.

The main product of this project is a top-level systems model of civilian chemical defense developed through the methodologies of Complex Adaptive Systems of Systems (CASoS) Engineering. Given the wide diversity in defense architecture components and the need for flexibility in the face of an ever-evolving threat, we argue that an effective defense architecture should exhibit the hallmark features of a CASoS: emergent behavior, self-organization, and adaptability.

Defending against chemical attack is unique. As a result, general weapons of mass destruction defensive strategies may be ineffective for chemical defense or have cascading impacts that result in no net benefit to the nation. The overall effectiveness of defensive measures can only be observed with an end-to-end perspective of the entire chemical defense system. We hypothesize that a top-level chemical defense model developed based on CASoS engineering is the most effective approach to account for these parameters. We will 1) contribute to the methodology development of CASoS and 2) provide a tool to improve our approach to chemical defense.

Summary of Accomplishments:

Through this project, we were able to develop novel approaches to studying chemical terrorism. Using methodologies derived from CASoS engineering, we created a high-level, analytical model of the chemical terrorism system of systems. This model is based on the timeline of events leading up to and following an attack. The adversary framework, which models the actions and decisions of the adversary, is one aspect of a larger system of systems model. The defense architecture, which models all defense activities related to chemical terrorism, is incorporated in parallel to the adversary framework. By concurrently modeling both the adversary and the defense in the chemical terrorism model, the interactions and influences between the two can be studied in order to elucidate the behavior of the chemical terrorism system as a whole.

The high-level, analytical model serves as a platform for developing and integrating multiple quantitative or semi-quantitative submodels. A wide variety of submodels could potentially be used to investigate specific interactions represented in the qualitative, analytical model. In this project, four types of submodels were investigated to demonstrate the integration of submodels within the overall system of systems model. These include a system dynamics model, an influence matrix, a game theoretic model, and an agent-based scenario model. Each of these submodels provides a unique lens through which the same set of system interactions can be studied. Assimilation of results collected with each submodel into the high-level CASoS model provides new depth and dimension to our

understanding of the chemical terrorism system. This two-tiered analysis approach has proven to be an effective means of integrating our chemical defense analysis efforts across multiple projects.

Significance:

Currently within DHS, there are multiple parallel efforts to develop chemical defense resources and capabilities. This research has provided a comprehensive systems model of chemical terrorism events that will permit optimization of chemical defenses via insights gained by examining various overall defensive postures.

Development of Chemiresponsive Sensors for Detection of Common Homemade Explosives

149568

Year 3 of 3

Principal Investigator: C. M. Brotherton

Project Purpose:

Homemade explosives (HMEs) represent one of the most challenging threats from which both the public and the military must be protected. HMEs can be synthesized using commonly available chemicals, and one of the most dangerous threats is HMEs made with peroxides. This project focused on developing a new sensor capable of detecting peroxide-based HMEs. The sensor technology is a polymeric chemiresponse sensor. The sensor consists of aligned conductive particles embedded in a polymer monolith. Upon exposure to the analyte, the polymer swells, causing the embedded particles to separate, thus providing a change in conductivity. Previous work at Sandia using this technology focused on detecting organic solvents. This project expanded the capability of these sensors by utilizing polymeric materials that are sensitive to peroxides. This project investigated a variety of embedded particle types, sizes, and configurations to study and understand the kinetic response of the polymeric materials to analytes in the gaseous phase. At the conclusion of this project, a sensor design was identified for sensing peroxides in the gas phase.

Summary of Accomplishments:

We have successfully developed a peroxide-sensitive material for use in a peroxide-based homemade explosive sensor and incorporated the peroxide-sensitive material into an inexpensive sensor platform utilizing chemiresistors. Typically, the chemiresistors under investigation are not sensitive to polar molecules such as hydrogen peroxide or water. We identified six different materials expected to interact with hydrogen peroxide. Experiments were performed to determine how to incorporate the six identified materials into a polymer matrix of polydimethylsiloxane (PDMS) and produce a stable polymer. Of the six, one of the materials developed demonstrated sensitivity to hydrogen peroxide and has been incorporated in a chemiresistor capable of detecting hydrogen peroxide vapor. The final sensor consists of PDMS and allyl methyl sulfide (AMS). The PDMS/AMS sensors demonstrated a significant response to hydrogen peroxide/water vapor at concentrations relevant to homemade explosives. When exposed to hydrogen peroxide, the AMS reacts to form sulfoxides and sulfones that lower the hydrophobicity of the sensor resulting in increased swelling and an increase in resistivity. Additionally, experiments were performed to optimize the formulation of the sensor materials, the quantity of conductive particles, and the operating conditions in order to maximize the production of sulfoxides and sulfones as well as reduce the reaction time.

Significance:

The end result of this project is a chemiresponsive sensor optimized for detecting hydrogen peroxide vapor at concentrations relevant to homemade explosives. By successfully accomplishing the purpose of this project, Sandia has developed a new capability that can benefit both DHS and DoD. The development of biaxially aligned magnetic particle/polymer composites as sensor elements also aligns with DOE goals for scientific discovery and innovation.

Extending Algorithms for Pattern Detection in Massive Data Sets to Commodity Cloud Platforms

151312

Year 2 of 2

Principal Investigator: T. Plantenga

Project Purpose:

The goal of this project is to develop advanced algorithms for use in mining data. The proposed work builds on specific Sandia expertise to address issues of national concern.

Massive amounts of data (terabytes to petabytes) are now collected in many applications of significance to national security, including Internet traffic, border security, and biological sensors. Analysts need tools that can process huge volumes of data to find interesting patterns and anomalies. The project focuses on tensor decomposition and subgraph isomorphism tools, an expanding area of research where Sandia is already a recognized world leader.

The novel feature of this project is to push advanced algorithms into commodity cloud computing environments, where massive data sets are increasingly likely to be located. This area is dominated by open source software and hardware architectures that differ significantly from high-performance supercomputing environments. The project considers commercial clouds (Amazon, Google), clusters of dedicated PCs, and specialized software paradigms (Hadoop, MapReduce). Commodity clouds are relatively cheap, highly scalable in terms of data storage, and may provide the only storage option for certain business cases. The challenge is to develop scalable methods appropriate for this environment.

A major innovation of this project is to extend tensor decomposition and subgraph isomorphism methods to run in a commodity cloud environment. Current methods address combined data sets of only about one gigabyte on a single machine, and little work has been done to utilize parallel processing. Advanced algorithms must scale to terabytes of data stored across thousands of machines in commodity clouds. Another innovation is to formulate national security applications as tensor models and typed graphs, and find conditions where advanced data mining algorithms apply. Success stories in the literature exist, but applications suggested for this project differ substantially from studies found in the literature.

Summary of Accomplishments:

1. We developed new algorithms for subgraph isomorphism matching in huge application graphs.
2. Performance was demonstrated on a graph with 100-billion edges, two orders of magnitude larger than any published result.
3. We created software for managing distributed graphs in clusters running the popular open source software, Apache Hadoop. Software was written to extract graphs from data, generate statistical characterizations, and identify statistical outliers and anomalies.
4. We made algorithmic improvements to tensor factorization methods for analyzing multidimensional data sets. Advanced optimization techniques were applied to core subproblems. Preliminary results indicate at least an order of magnitude improvement over the state of the art.
5. We applied graph algorithms to DNA sequencing data to help identify anomalous genomes. The goal was to improve results for the difficult problem of sequencing metagenomic data that mixes DNA from many organisms.
6. We applied tensor methods to fuse kinase-ligand simulation data with experimental measurements. A coupled tensor approach with clustering was applied to fuse while controlling the relative emphasis placed on the data sets.

7. We developed new performance analysis tools for Hadoop MapReduce jobs. The tools are generally useful for MapReduce jobs, and were particularly useful for improving the subgraph isomorphism algorithm of this project.
8. We developed novel visualization tools for large graphs and tensor results. Existing workstation graph tools scale poorly beyond 10,000 nodes, and no general-purpose tensor visualization tools exist. The new work provides building blocks to address these shortcomings.

Significance:

We produced a MapReduce subgraph isomorphism algorithm that has been productionized for a follow-on customer. We made algorithmic advancements in tensor decomposition and MapReduce data handling that will be useful. The combination of algorithmic science with application domain experts created awareness in both groups of people that should yield dividends for several agencies involved in data mining, such as DHS.

Refereed Communications:

T. Plantenga, Y.R. Choe, and A. Yoshimura, “Using Performance Measurements to Improve MapReduce Algorithms,” in *Proceedings of the International Conference on Computational Science (ICCS)*, pp. 1920-1929, 2012.

T. Plantenga, “Inexact Subgraph Isomorphism in MapReduce,” to be published in the *Journal of Parallel and Distributed Computing*.

Using Fast Neutron Signatures for Improved UF₆ Cylinder Enrichment Measurements

151315

Year 2 of 3

Principal Investigator: S. Kiff

Project Purpose:

One of the most important problems in nonproliferation is monitoring the degree of enrichment from uranium enrichment plants. Centrifuge enrichment plants are necessary to produce fuel for commercial power plants but are also capable of producing highly enriched uranium, which can be configured into a nuclear weapon. Existing technologies for measuring U-235 enrichment in a UF₆ cylinder require controlled conditions for accurate measurements. Low-energy neutrons and gammas used by current technologies have short penetration through dense UF₆, and since the UF₆ thickness near the measurement location is not known a priori, the current measurement techniques are insensitive to UF₆ in the center of the detector. Thermal neutron counting rate near a cylinder can vary by as much as 50%, depending upon the solidified geometry and the cylinder orientation relative to the detectors.

Our project applies fast neutron spectrometry and imaging to ascertain the UF₆ enrichment inside the cylinder. Deeply penetrating fast neutrons allow measurements that are sensitive to materials throughout the entire cylinder. Imaging the UF₆ material distribution within the cylinder allows compensation of geometry-dependent measurements when the UF₆ mass is unevenly distributed.

This proposed UF₆ cylinder imager is unlike any other enrichment monitor: neither neutron spectrometry nor fast neutron imaging has been applied to UF₆ cylinder enrichment measurements. Technical risks are that the neutron spectrum may degrade via scattering such that spectrometry becomes impossible; also, the benefits of imaging are unknown at this time. If successful, this project will produce an enrichment measurement technique that is more accurate and more sensitive to diversion scenarios than current technologies.

Open Source Information Verification 151316

Year 2 of 2

Principal Investigator: K. E. Horak

Project Purpose:

The growing number of peaceful nuclear activities globally will increase the amount of nuclear material and sites that must be inventoried, tracked, and protected under safeguards by the International Atomic Energy Agency (IAEA) and analyzed by other agencies. The anticipated growth of nuclear-related activities and materials will increase the resource demand on various agencies. Geographic information system (GIS)-based tools are currently being developed for use in a wide variety of nuclear safeguard activities including site inspection, verification, and wide-area environmental sampling. This work seeks to test the hypothesis that analysts will more frequently and effectively utilize geographic information if provided with easily trainable, interoperable tools designed to systematically extract and store geospatial data from the Internet. Because of the complex nature of geospatial data, this capability will require that a diverse set of technological tools be integrated into a single package designed to integrate into the analyst's existing workflow.

Summary of Accomplishments:

Foremost among our accomplishments was the verification of our hypothesis that by providing a structured search framework for exploring and gathering open-source information, this project gives analysts in a wide variety of domains an easy-to-use toolset and strategy for collecting and visualizing geospatial aspects of their research. We discovered that in a sample of analysts from Sandia, having a browser-based geospatial tool and a defined search strategy enabled them to quickly learn to make use of geographical information within their text document collections.

Finally, a beneficial side effect was the creation of the GeoSafeguards tool, which enables analysts with only minimal training to quickly and easily create maps based on the automatic extraction of place-names for collections of digital text documents.

Significance:

Once open-source document collections are assembled, analysts can create meaningful first-cut maps from the place-names contained within, a task once reserved for highly trained GIS experts working with expensive software. This frees GIS experts for more advanced and difficult analyses. By making geospatial information accessible to analysts in agencies such as DOE/NNSA, they can more quickly and more confidently answer pressing national security questions.

Refereed Communications:

M. McDaniel, D. Bleakly, and K. Horak, "Open-Source Geospatial Information and Tools for Safeguards Analysts," in *Proceedings of the 53rd Annual Meeting of the Institute of Nuclear Materials Management*, 2012.

Human Cargo Detection via a Microfabricated Pulsed-Discharge Ionization Detector

151318

Year 2 of 2

Principal Investigator: R. P. Manginell

Project Purpose:

Humans are often clandestinely transported across borders to facilitate illegal immigration or maleficent intentions. What is required is a portable, low-power detection system that can easily be operated at checkpoints and border crossings around the world. This program will demonstrate the use of a pulsed discharge ionization detector (PDID) for use in detecting signatures of both human cargo and contraband compounds. In parallel, we will demonstrate for the first time an ultraminiaturized PDID.

A variety of chemicals have been identified as unique indicators of human presence. Field detection of relatively small amounts of chemicals against a high background of interfering compounds represents a great technical challenge. Given these difficulties, a gas chromatograph (GC)-based sensing system coupled with a highly sensitive general detector like the microPDID will be required to realize an appropriate sensing system.

This project is tackling the difficult task of scaling a PDID to ultraminiature dimensions. A micro-PDID system does not require vacuum pumps like a micro-mass spectrometer, and thus would be simpler and more rugged, while still being able to detect the same range of target analytes. We are demonstrating the technical feasibility of such a system and undertaking the development of a miniature prototype.

Summary of Accomplishments:

This project includes a broad spectrum of volatile organic compounds (VOCs) for wide ranging applications. The PDID is a low-power, universal detector, requiring no vacuum pump. We employed COMSOL multiphysics (COMSOL, Burlington, MA) and SIMION[®] (ion/electron optics simulation) modeling for designing and understanding the operation of our prototype scalable mini-PDID. In this project, we tested the performance metrics of a commercial PDID and the mini-PDID for sensitive detection and quantitation of several exemplars of chemical, biological and explosive threat agents at parts-per-billion and parts-per-trillion levels.

In conclusion, we made tremendous progress upon all stated goals in the project. In fact, we expanded the scope of the investigations to extend the applications of a commercial PDID and the Sandia mini-PDID.

Significance:

The mini-PDID is a near universal detector and can be integrated with micro gas chromatography components to create enhanced field detection hardware for national security applications. We have demonstrated detection of materials directly relevant to national security missions of DHS. Detection of greenhouse gases is also now seen as a national security issue and is part of the climate mission of DOE. We have also studied the scaling of the PDID detector, in addition to the work mentioned above, for the benefit of advancing the frontiers of science and engineering.

Predictive Modeling of Non-Ideal Explosives

151321

Year 2 of 3

Principal Investigator: R. G. Schmitt

Project Purpose:

Nonideal explosives (NXs) behaviors are not well represented by classical detonation theory and scaling laws, and relatively little fundamental research has been conducted to characterize their performance and predictive numerical modeling is largely absent. An improved level of understanding will rely on the tightly coupled pursuit of experiment, theory, and numerical modeling. Numerical modeling is essential for the discovery of reaction mechanisms and simulating the coupled, nonlinear evolution of composition, temperature, and pressure of the reactive flow behind a shock front in highly heterogeneous media. Novel and systematic experimental research is required to characterize important phenomena relating to the high-pressure equation of state and shock behavior. Experimental and numerical research is required to advance the theoretical understanding upon which an appropriate numerical model and methods to solve the model are constructed. NXs do not follow ideal scaling laws and do not have a classical TNT equivalence. The new modeling approach pursued in this project addresses these shortcomings.

Desorption Electrospray Ionization–Differential Mobility Spectrometry (DESI-DMS) for Homemade Explosives Detection

151322

Year 2 of 2

Principal Investigator: C. L. Rhykerd, Jr.

Project Purpose:

An investigation of a new trace detection method is being pursued. There is potential to detect a much larger analyte list (hundreds as compared with approximately ten) than conventional trace methods (such as ion mobility spectrometry) by integrating a desorption electrospray ionization (DESI) source with a differential mobility spectrometer (DMS). Investigations will focus on homemade explosive chemicals (explosives, oxidizers, fuels, and precursor chemicals). DESI-DMS has not been studied previously.

Fundamental scientific questions about the ionization and detection processes are the following:

- What is the efficiency of ionization as a function of swab material (cotton, steel mesh), angle of incidence, distance from the sample, and spray liquid (water, methanol)?
- What is the ion lifetime (longer lifetimes enable additional specificity)?
- What is the maximum resolution achievable (to reduce nuisance alarms and resolve similar molecules)?

Previous work has focused on either lab-only techniques (mass spectrometry) or a very short list of common high explosives. This work will anticipate terrorists' explosive choices by developing a method that is suitable for a wide range of explosive materials and that is fieldable for screening applications.

Summary of Accomplishments:

DESI-DMS was built and a range of explosive materials tested to determine the potential of the approach. A commercially available Prosolia DESI-DMS was mated to a New Mexico State University DMS for this purpose. The results were all negative. This is likely due to the low sensitivity of the differential mobility spectrometer (not enough ions produced) compared to mass spectrometry or due to the selected operational parameters of the DESI ionization source. Some positive results were obtained for paper spray ionization coupled with an ion mobility spectrometer (IMS). Paper spray is a novel and very simple approach from a hardware perspective, where a triangle of paper is held in an alligator clip and high voltage and a solvent applied to the paper. Positive results were obtained for explosives and some fuels. This is a small advantage (ionizes some fuels) in the number of analytes ionized and detected with a paper spray ionization–IMS. We learned that the paper spray approach merits further study. Paper spray samples are much simpler to prepare, and the addition of the drop of solvent at the back of the paper triangle could easily be automated or a manual dropper provided. One can imagine a paper spray ionization–IMS system for field detection of explosives and homemade explosive precursors. That system could have a larger number of detectable analytes of interest than traditional ion mobility systems with Ni-63 ionization, but will still fall short of the very large list of potential homemade explosive precursors. We identified a better option: paper spray ionization–IMS, but not a solution to the homemade explosive trace detection problem.

Significance:

This technology could significantly expand the number of analytes we could detect with trace techniques, thereby contributing to the mission of DHS and other agencies.

Genomics-Enabled Sensor Platform for Rapid Detection of Viruses Related to Disease Outbreak

151324

Year 2 of 3

Principal Investigator: S. M. Brozik

Project Purpose:

Infectious diseases pose growing threats to our nation. Disease outbreaks are a challenge to detect. The development of more rapid diagnostic assays for virus detection with high sensitivity and specificity will be very useful for the management and treatment of patients, and for epidemiological surveillance. Viruses can be isolated from the blood of someone during early stages of infection, before antibodies can be detected. However typical methods for detection involve virus isolation through tissue culture assay with long incubation periods of a week. Molecular diagnostic systems for RNA detection are much faster but still require time-consuming steps and are not yet portable. We propose ultrasensitive, direct, hybridization-based RNA detection systems, requiring small sample sizes and short detection times for field and clinical use. Though detection of RNA is difficult because of its lack of stability and extraction from the virus, the payoff of a high-throughput screening capability during emergency response or outbreaks is enormous for public health. Two independent assays will be developed to address the many challenges of RNA detection. We will also take advantage of the recent explosion of genomics data on many arboviruses, including several of those widely considered most important to public health and national security, providing a novel opportunity to leverage this data for diagnostic benefit as well as biothreat detection.

High-Energy Resonance Radiography by Double Scatter Spectroscopy 151325

Year 2 of 3

Principal Investigator: P. Marleau

Project Purpose:

This year, Monte Carlo modeling and design and laboratory-scale tests have helped identify and validate choices for the design of a demonstration detector. A segmented scintillator block in front of four photomultiplier tubes (PMTs), guided by early promising modeling results using Geant4 Monte Carlo was tested. Various groove materials as well as outer surfaces were tested. Teflon filled grooves performed better in terms of position resolution. However, a single non-segmented block also performed very well. Interaction positions are reconstructed using the ratios of light collected in each PMT to the total light, a method known in the medical imaging community as Anger Logic. However, unlike traditional Anger Logic, we used maximum likelihood expectation maximization (MLEM) methods capable of reconstructing the depth of interaction (z-position) to avoid reconstruction artifacts. We designed a high-position and -timing resolution, low-channel-count detector array. The detector block contains a minimum of excess inactive material to minimize scattering and consists of a hexagonal arrangement of seven 3-inch photomultipliers coupled to a single volume of scintillator. In addition to the detector, a data acquisition system was designed that consists of a single commercial 8-channel, 250 MHz, 12-bit digitizer for each detector block (6 blocks for the entire imager). Using a coincidence trigger, waveforms will be read out for offline analysis for position, energy, and time reconstruction using MLEM methods. Custom high-voltage power supplies have been built into the detector blocks for increased safety and reduced cabling (user friendly concept). The first blocks have been built and will be ready to test in early FY 2013.

Enhanced Micellar Catalysis 151326

Year 2 of 2

Principal Investigator: R. Betty

Project Purpose:

Sandia's DF-200 decontamination formulations are a proven, rapidly effective solution for decontamination of chemical/biological warfare (CBW) agents. However, little is known about the fundamental mechanisms of micellar catalysis that enable this successful CBW decontamination chemistry.

Understanding the micellar geometry and physical characteristics of the standard DF-200 formulation before and after exposure to an agent-challenged environment will lead to new decontamination formulations with enhanced-performance broad-spectrum decontamination. Current deployment methods will benefit from the incorporation of enhanced micellar catalysis knowledge, demonstrated by increased efficiencies in capacity and neutralization. The end goals are to use less material for decontamination to minimize logistical burdens and to enable more rapid kinetics of DF-200 formulations.

During the first year of this project, we discovered that the technical challenges for characterization were greater than anticipated. The planned approach of using in situ light scattering techniques to characterize the formation of cationic micellar and vesicular environments was precluded by inherent effervescence and by analysis limitations due to high viscosity of the initial control test solutions. It has become necessary to use more advanced technologies including both small angle x-ray scattering (SAXS) and cryogenic-transmission electron microscopy (cryo-TEM) to interrogate the micellar environment. As a consequence of Sandia's current limitation in expertise and instrumentation required to accomplish these technical tasks, external partnering has been initiated with the University of Minnesota (UMN) characterization facility.

A key task for this project has been to apply the characterization information to improve decontamination kinetics for deployment methods such as the charging of aerosolized DF-200 droplets. A new aerosol test chamber has been designed and fabricated, and a test approach was developed.

Summary of Accomplishments:

We established baseline micellar characterization data for DF-200 and developmental decontamination liquids through SAXS and pulse field gradient nuclear magnetic resonance (PFG NMR) techniques. PFG NMR was highly useful for the measurement of diffusion properties of key surfactants and the impact to surfactant micelle size/shape upon addition of formulation components. The partitioning of an organophosphate compound in key surfactant solutions and at various concentrations was measured. Diffusion properties of surfactants in various solution mixtures were measured to infer potential phase changes. In total, diffusion properties of various decontaminant materials will be contrasted to agent efficacy both in solution and on surfaces to reduce desirable micelle properties and reactive formulation components.

We improved our understanding of rotary-atomized droplet chemistry characterization analysis requirements. For a limited set of rotary atomization nozzle conditions, exponential droplet rate losses were determined for low and high relative humidities. We developed an altered technical approach for future decontamination developmental projects. Future R&D will focus on first obtaining an increased

knowledge base of fundamental transport issues (thorough characterization of material matrices and agent/simulant binding phenomenon) supported by in-situ monitoring and transport modeling. NMR micelle partitioning studies will inform cause and effect relationships as components are mixed to form reactive decontaminant solutions. The performance of modified decontaminants must be assessed, transitioning from standardized protocols to protocols that adequately achieve realistic deposition of agent and decontaminants; subsequent analysis of the recovery of unreacted agent above, within, and removed from contaminated surfaces is then necessary to comprehensively determine decontamination performance. We anticipate that live agent efficacy results (performed outside of the project) can be compared with NMR diffusion properties to efficiently inform cause and effect relationships of constituents across various formulations. This knowledge will be used for current and future decontamination development efforts.

Significance:

The results of this project have benefitted the national security missions by significant improvements to Sandia's CBW response capabilities across a wider variety of release scenarios. The insight from this work allows the more rapid evolution and optimization of decontamination formulations and applications. It will improve Sandia's ability to respond to surface decontamination challenges for DHS and other agencies.

Simulation-Based Strategic Analysis of Complex Security Scenarios 154570

Year 2 of 2

Principal Investigator: Y. Vorobeychik

Project Purpose:

Many advanced technical tools are available to prevent attacks on national infrastructure. The complex interplay between individual incentives and global (organizational and/or national) goals can be modeled and analyzed using game theoretic techniques. By analyzing not only what is possible, but also what is motivated by specific scenarios, a holistic approach to security problems can be developed, informing policy and providing tools to policy makers. This research will advance game theoretic modeling and analysis of problems related to security domains, such as cybersecurity. The goal of the project is to construct realistic game theoretic models that unify several current incentive-based approaches to security, and develop simulation-based methods for analyzing such models that exploit the high-performance computing capabilities at Sandia. Such a general model formulation will marry large-scale simulations of realistic systems to game-theoretic analysis. We will focus on the behavior of game theoretic solutions with system scale, structure of interactions between players, and response to policy instruments (e.g., subsidies, penalties, etc.).

Summary of Accomplishments:

We analyzed interdependent security settings and demonstrated how to compute and approximate optimal security policies when assets are interdependent. We also studied adversarial patrolling scenarios. In certain highly structured settings, we showed that our approaches are highly scalable and far superior to state-of-the-art alternatives.

Our final contribution is a general abstract framework for quantitative analysis of trust and risk. Specifically, we formally define both trust and risk in very general terms, and show that in very limited settings, our definition of risk recovers the usual notion that is commonly used; however, this also demonstrates the limitation of currently used notions of risk. Moreover, we use the formal definitions of trust and risk to construct, first, a decision-theoretic and, subsequently, a game-theoretic framework for optimally mitigating risk in security settings.

Significance:

We provide novel optimization approaches that explicitly account for mitigation strategies. The game theoretic framework uniquely enables a principled analysis that is applicable to security situations faced by NNSA and numerous other agencies.

Refereed Communications:

S. Judd, M. Kearns, and Y. Vorobeychik, "Behavioral Conflict and Fairness in Social Networks," presented at *Workshop on Internet and Network Economics*, 2011.

Y. Vorobeychik, "A Game Theoretic Bidding Agent for the Ad Auction Game," presented at *International Conference on Agents and Artificial Intelligence*, 2011.

Y. Vorobeychik, D.M. Reeves, and M.P. Wellman, "Constrained Automated Mechanism Design for Infinite Games of Incomplete Information," *Autonomous Agents and Multiagent Systems*, vol. 25, pp. 313-351, 2012.

M. Kearns, S. Judd, and Y. Vorobeychik, "Behavioral Experiments on a Network Formation Game," presented at *ACM Conference on Electronic Commerce*, 2012.

B. An, D. Kempe, C. Kiekintveld, E. Shieh, S. Singh, M. Tambe, and Y. Vorobeychik, "Security Games with Limited Surveillance," presented at *National Conference on Artificial Intelligence*, 2012.

Y. Vorobeychik and S. Singh, "Computing Stackelberg Equilibria in Discounted Stochastic Games," presented at *National Conference on Artificial Intelligence*, 2012.

J. Letchford and Y. Vorobeychik, "Computing Optimal Security Strategies for Interdependent Assets," presented at *Conference on Uncertainty in Artificial Intelligence*, 2012.

Y. Vorobeychik, J.R. Mayo, R.C. Armstrong, and J. Ruthruff, "Noncooperatively Optimized Tolerance: Decentralized Strategic Optimization in Complex Systems," *Physical Review Letters*, vol. 107, p. 108702, September 2011.

Multi-Objective Optimization Approach for Multimodal Information Retrieval **154694**

Year 2 of 2

Principal Investigator: B. S. Paskaleva

Project Purpose:

A principal goal of multimodal information retrieval (MMIR) is extraction of relevant information from large heterogeneous databases. To this end, users' information needs are abstracted into sets of formal queries and databases are ranked by similarity functions, which compare queries against each database.

A key open problem in MMIR is the development of similarity functions that maximize the relevance of the ranking with respect to a user's information needs, while minimizing the probability of error. Because different similarity functions expose different aspects of the match between the database and the queries, we propose to rank the database using a superposition of similarity functions, optimized with respect to utility measures expressing relevance.

To address MMIR challenges, we propose a two-stage approach, which draws upon ideas from optimization, control, and approximation theory. The first stage aims to establish a formal methodology for maximization of ranking relevance by formulating the task of finding optimal superposition of similarity functions as a reference multi-objective constrained optimization in Banach spaces. The second stage focuses on the approximation of the reference problem by finite-dimensional convex optimization problems or linear programs, which can be solved efficiently.

Lifting of MMIR into an abstract setting separates our approach from existing methodologies that are often dominated by ad hoc or problem-specific algebraic techniques. In so doing, we aim to discover basic design principles that can be adapted to solve diverse MMIR problems. Therefore, if successful, this effort will support the core mission of Sandia and its future growth in these areas. Our previous experience and collaborations with leading researchers in classification, pattern recognition and optimization gives us confidence that we will be able to complete the project.

Summary of Accomplishments:

We focused on several key tasks, which establish foundations for the development of methodology that enables extraction of relevant information from large heterogeneous databases. We developed a consistent extension of similarity functions that bridge the standard vector space model (VSM) with the set-based similarity approach. We demonstrated that properly augmented VSM provides an abstraction for a broad class of information retrieval approaches. The performance of the extended similarity measures is compared by solving an entity-matching (EM) problem for two types of benchmark datasets. Among other things, our results show that the new similarity functions perform particularly well on tasks involving matching of records by keywords.

The extended vector space model (EVSM) served as foundation for mathematically rigorous definition of the EM problem. We developed a supervised EM framework that interprets the EM as the combinatorial optimization problem of finding the maximum weight matching in a weighted bipartite graph connecting records from two databases, also known as Linear Sum Assignment Problem (LSAP). The casting of EM problems into LSAP offers valuable practical and theoretical advantages. There are efficient algorithms that solve LSAP in polynomial time. Availability of such algorithms reduces the task of solving the EM problem to computing weights for the edges of the bipartite graph connecting the records from the databases. This allowed focusing efforts on the development of robust and flexible

methodologies for the estimation of the similarity between records and led to the notion of an optimal similarity function (OSF) for MMIR problems. The OSF is sought as a linear combination of similarity functions for the common relation attributes. Solution of a suitably defined quadratic program using training data defines the weights in the linear combination. Computational studies using the Abt-Buy e-commerce database and publication databases composed of research articles confirm the robustness of our approach.

Significance:

Homeland, energy, and infrastructure securities lead to challenging information retrieval problems. Application to prototype MMIR problems with national security ties is relevant to Sandia's mission and to the mission of DOE and other agencies. Our work resulted in a mathematically precise augmentation of VSM and robust and flexible algorithm for EM that provided an abstraction for a broad class of information retrieval approaches and can be adapted to various application contexts. Research results provide Sandia with rigorous foundation for MMIR capabilities supporting its national security mission and enable future growth and expertise in the area.

Exploring the Development of Large-Area Geiger-Mode Avalanche Photodiodes 154936

Year 2 of 3

Principal Investigator: S. Soisson

Project Purpose:

There is an interest in developing a technology that has a lower power requirement than a traditional photomultiplier tube (PMT) but delivers the same photon sensitivity as the PMT. Studies in silicon avalanche photodiodes operated in Geiger-mode (G-APD) with many pixels show promise for an effective PMT replacement. The G-APD shows many similarities to the PMT such as high gain and excellent photon sensitivity, but offers the advantage of having a lower power requirement. However, the size of available G-APDs is only 6 mm². This is not appropriate for replacing a PMT when large active areas are needed. In this project, we are exploring the development of large-area G-APDs.

Characterization of Atmospheric Ionization Techniques for the Identification of New Chemical Signatures from Homemade Explosives in Complex Matrices

156400

Year 2 of 3

Principal Investigator: J. M. Hochrein

Project Purpose:

Desorption Electrospray Ionization (DESI) and other atmospheric ionization techniques coupled with mass spectrometry offer distinct advantages over traditional detection systems because of the extremely diverse range of detectable compounds, vastly improved specificity, high throughput, fieldability, and little to no sample preparation.

Although DESI has been demonstrated on some target compounds, significant technical challenges and opportunities associated with the method exist. First, there are many operational parameters that need to be optimized such as solvent selection, ionization energies, surface material selection, and identification and reduction of background contaminants. Second, many of the target compounds are analyzed as “neat” samples in very controlled environments under optimum conditions, which are often very different from those in the field. In addition, many analytes of interest have not been investigated to understand if they are amenable to ambient detection.

This research focuses on enhancing scientific understanding of DESI and other atmospheric ionization techniques. Information on specific ions can then be used to enhance the effectiveness of existing technologies including ion mobility spectrometry (IMS) and differential ion mobility.

Development of a Sustainable Anthrax Diagnostic Test for Countering the Biological Threat

158813

Year 1 of 3

Principal Investigator: M. Finley

Project Purpose:

Anthrax poses a significant threat to US National Security as demonstrated by the 2001 terrorist attacks targeting the US Postal Service and Hart Senate Office Building. The causative agent, *Bacillus anthracis*, is ubiquitous, and more importantly, found in countries harboring terrorists. Anthrax commonly causes sudden death in livestock, and consequently, is routinely isolated and propagated by indigenous populations to diagnose the disease. We propose to develop a sensitive diagnostic assay that will significantly reduce the amount of *B. anthracis* maintained in laboratories. The assay will use the sensitivity and cost effectiveness of culture, without producing viable cultures; samples will be decontaminated after testing is complete. The project will develop a practical and deployable diagnostic assay that minimizes *B. anthracis* handling and mitigates the proliferation risk.

The goal of the proposed work is to develop a portable diagnostic device for *B. anthracis* detection, for use in developing countries where the biological threat is significantly elevated. Currently, commercially available diagnostics such as the TetraCore BioThreat Alert-test strips are relatively expensive (~\$40 per assay with control) and additionally require culturing of the target organism prior to the assay. In contrast, our proposed device will cost <\$5 per assay, require no power or instrumentation/equipment to operate/interpret the test result, be operable by individuals with little or no technical training, and apply chemical and phage technology to sterilize the contents of the culture. Moreover, the self-contained device will combine micro-culture methods to amplify *B. anthracis* with plasmon coupling among metal nanoparticles for improvement of target detection limit by several orders of magnitude.

Advance Diagnostic and Sample Preparation Platform for Early Threat Surveillance

158814

Year 1 of 3

Principal Investigator: S. Branda

Project Purpose:

Emerging infectious diseases present a profound threat to global health, economic development, and political stability and, therefore, represent a significant national security concern for the US. The increased prevalence of international travel and the increase in globalized trade further amplify this threat. The key to preventing an outbreak before it goes global is to establish a biosurveillance network that effectively reaches even the most remote regions and provides a network-integrated, location-appropriate diagnostic capability. At present, the two main factors that prevent the extension of biosurveillance activities beyond centralized laboratory facilities are the lack of a deployable rapid-response diagnostic platform and a method to safely and consistently process infected samples in the field for analysis.

To minimize serious global outbreak events, modern surveillance requires both coordination and investment in infrastructure at the international level to enable rapid response to pathogens as they emerge. The first critical steps in the surveillance process (clinical observation, sample collection, preliminary diagnosis) typically fall to first responders around the world. However, the facilities, technology, and protocols they use can vary widely depending on the available infrastructure, which complicates efforts for a globally coordinated biosurveillance scheme. This project proposes to address this identified capability gap by delivering an automated clinical sample processing platform integrating a “universal” sample collection and preparation protocol with a comprehensive diagnostic strategy. This will require: 1) creation of a fieldable advanced diagnostic and sample preparation (ADSP) platform to safely and cost-effectively automate the extraction of pathogenic nucleic acids (NA) from potentially infectious clinical samples for analysis, 2) on-platform multiplexed polymerase chain reaction (PCR) assays for initial point-of-care screening for usual-suspect pathogens, 3) on-platform NA formatting for subsequent off-platform microarray or second-generation sequencing (SGS) analysis, and 4) transfer of the ADSP technology to key collaborators for testing and integration into real-world biosurveillance workflows.

Development of a Statistically Based Access Delay Timeline Methodology 158816

Year 1 of 1

Principal Investigator: W. G. Rivera

Project Purpose:

The charter strategy for “adversarial delay” is to hinder access to critical resources through the use of physical systems designed to increase an adversary’s task time.

The traditional method for characterizing access delay has been a simple model focused on accumulating times required to complete each task with little regard to uncertainty, complexity, or decreased efficiency associated with multiple sequential tasks or stress.

The delay associated with any given barrier or path is further discounted to worst-case, and often unrealistic, times based on a high-level adversary. The result is a conservative calculation of total delay where all attack paths are considered viable in the minimum possible time.

We are pursuing a new methodology that considers the uncertainties inherent in the problem to develop a realistic timeline distribution for a given adversary path. By specifically considering uncertainty in adversary ability, tool set, breach time distribution, barrier effectiveness, human factors, etc., a model can be developed to represent the effectiveness of the delay system against various attack scenarios and threats.

This effort seeks to incorporate advanced statistical methodologies, taking into account small sample size, expert judgment, and threat uncertainty. The result will be an easy to communicate distribution of delay times directly relating to system risk, assisting the end user in making informed decisions while weighing benefits against risks, ultimately resulting in greater system effectiveness with lower cost.

Summary of Accomplishments:

We developed and demonstrated a methodology for calculating a statistical distribution for time required to complete a series of attack tasks using limited data sets, human factors, and non-empirical data.

The project combined Bayesian statistical methods with Markov Chain Monte Carlo computational techniques to analyze an adversary’s probability of success when executing abrupt attacks that lead to goals like theft or sabotage. In such scenarios, adversaries must complete a series of tasks before responders (e.g., police) can interrupt the attack. These tasks involve force, stealth or deception, and adversaries must remain undetected until they can confidently win the race against the responders. Data for task durations and detection probabilities are sparse, noisy, and often only partially applicable. Past analyses methods have produced highly conservative results without characterizing uncertainties. The methods developed in this project enable analysts to explicitly make use of all available experimental and analytical data, to compensate for human performance shaping factors (e.g., errors or duress), and to compute adversaries’ success probabilities within the context of a full uncertainty analysis. This eliminates analytical conservatism and provides decision makers with more complete data upon which to consider potential mitigation options.

While the current mathematical form of the research is not yet usable for day-to-day analysis, the algorithms and formulation should be applicable to advanced modeling analysis and eventually a computer tool for in-the-field analysts.

Future proposed work for this research is to utilize the algorithms and processes developed to create a computer tool that would conduct the math behind a comprehensive Graphic User Interface (GUI), allowing the analyst to focus on the security implications of an analysis, and not the methodology behind it.

Significance:

The primary goal of this research has been to develop a methodology to calculate timeline distributions to evaluate the implications of current and future access delay security system designs elements. Because the current method of delay time calculation often results in unnecessarily conservative timelines, this new methodology has sought to incorporate statistical methods to better predict actual delay, therefore reducing the conservativeness of the calculation. The end result is to allow the decision maker to better evaluate the system as a whole (detection, delay, and response) in order to distribute resources in a more efficient and cost-effective manner. Thus, the research outcomes should be of use to multiple agencies that deal with the use of adversarial delay as a protective mechanism, including, for example, DoD and DHS.

Multi-Target Camera Tracking, Handoff, and Display

158819

Year 1 of 3

Principal Investigator: R. J. Anderson

Project Purpose:

For operators, the manual tracking of intruders takes focus and attention away from overall situational awareness. By combining automated tracking algorithms that share target information across multiple cameras, we can radically simplify the human/machine interface and shift the cognitive focus from manual operation of the system to command and control. Operators designate targets and the system keeps track of them throughout the engagement. All targets will be displayed on a single coherent display system that links tracked intruders in a compound to the respective video feeds. The key breakthrough is a revolutionary new technique in feature-based tracking and adaptive learning. We will adapt and augment this approach, develop complementary hand-off techniques, and create a system that can track multiple targets with multiple cameras. Applications include fixed infrastructure sites and tactically deployed surveillance systems.

Our focus will be on adapting this approach to facility protection tasks that incorporate multiple cameras and track multiple targets. Although the detectors used in some applications have proved insufficiently robust for multiple camera handoffs, modifications to the algorithm that incorporate color information and depth modeling are showing promise. The resulting system will use a 3D model of camera and building locations, improved invariant feature detectors, a Bayesian framework for predicting motion of 3D targets, and innovative methods for handing off tracking information between cameras and processors.

Rapid Affinity Reagent Development for Emerging Pathogen Detection

158820

Year 1 of 2

Principal Investigator: C. Koh

Project Purpose:

We face constantly emerging and naturally occurring global biological threats. In the event of disease outbreak, fast and sensitive diagnostic tools deployable to multiple point-of-care (POC) locations are crucial for effective biosurveillance and crisis management. Rapid antigen-based tests, which are the most amenable approaches to POC diagnostics, typically employ antibody affinity-capture schemes for pathogen detection. However, antibody production relies on hybridoma technology (i.e., antibodies are not very stable to storage) especially in resource-poor areas lacking refrigeration. Polymerase chain reaction (PCR) approaches require extensive sample preparation and are very expensive because of thermal cycling needs. Thus, there remains a critical need for versatile POC diagnostic approaches that are rapidly reconfigurable and deployable in emerging pathogen outbreak scenarios.

Here, we propose to improve biological emergency responsiveness by employing Sandia's virus-like particles (VLPs) as rapidly deployable affinity reagents. VLPs have shown efficacy in cell targeting and drug delivery applications; this project will pioneer their use as diagnostic affinity reagents. VLPs require short times for development with affinities for target analytes that rival commercial monoclonal antibodies. VLPs are less likely to denature and hence have much longer shelf life than antibodies. VLPs can also be loaded with cargo such as multiple quantum dots (QDs) facilitating a novel sedimentation assay directly targeting infectious agents using Sandia's centrifugal microfluidics platform. The proposed assay scheme will exceed the stringent limits of detection for emerging pathogens. This project merges two of Sandia's proven technologies to tackle the pressing challenge of emerging pathogen detection; the final product will vastly outperform state-of-the-art techniques.

Intrinsic Material Elements Seal 158821

Year 1 of 3

Principal Investigator: H. A. Smartt

Project Purpose:

Seals are widely used for identifying, securing, and monitoring items. They must be unique, not subject to counterfeiting, tamper indicating, robust, easily applied, and low-cost. Using newer technologies, better seal designs and readout options are possible. State-of-the-art cameras, modern image analysis, and new illumination approaches can be combined to produce a faster, user-friendly, non-contact readout system. This will reduce the time that inspectors spend in restricted or environmentally unfriendly locations.

We are developing a seal technology based on microscopic, randomly located and oriented reflective elements that possess planar optical cavities that vary from particle to particle. Each particle's reflectance spectrum depends on its cavity parameters, the local orientation of the particle, and the incidence angle of the interrogating beam. Designed to be easily applied in a coating or paint, this seal will be compatible with flat surfaces as well as complex rough geometries. Interrogation of the seal will include illumination with multiple wavelengths and multiple incidence angles, and will lead to a multivariate data cube that can be analyzed using efficient multivariate image analysis algorithms. This approach expands the information collected from seals beyond simple spatial locations and orientations of the particles, to include spectral and morphological attributes.

Modeling the Contents of Nuclear Weapons in Real-Time 161869

Year 1 of 3

Principal Investigator: G. G. Thoreson

Project Purpose:

The goal of this project is to discover new methods and algorithms for fast computational radiation transport. Traditional techniques rely on reducing the problem to one spatial dimension; if available, supercomputers can be used for two- or three-dimensional analysis. While a one-dimensional approach is fast enough for use in the field, there are known source configurations, which fail this simplification. Furthermore, the alternative approach requires supercomputers, which are impractical in a deployable environment. This project seeks to compromise the high fidelity of computationally expensive supercomputer simulations with the speed of one-dimensional solutions, allowing a field-deployable solution for complex source configurations. The approach relies on combining multiple one-dimensional solutions with ray-tracing techniques to compose an approximate solution. The use and accuracy of multiple one-dimensional solutions is not well understood, but preliminary tests show promise. The ultimate goal is to replicate high-fidelity transport simulation results in orders of magnitude less computation time.

Compressive Sensing for Nuclear Security Applications 161870

Year 1 of 3

Principal Investigator: B. J. Gestner

Project Purpose:

The purpose of the project is to explore efficient acquisition of photomultiplier tube (PMT) output signals.

We developed a MatLab toolbox for PMT output signal generation and pulse shape discrimination (PSD) processing. The toolbox implements the Marrone model and allows variation of pulse shape/dynamics through control of six empirical parameters, pulse start location, and signal-to-noise ratio (SNR). We also implemented various PSD methods, including the recently proposed frequency gradient analysis method (Novel Goertzel algorithm application). Lastly, we included functions based on recently proposed cross-correlation methods that extract both the start location and delivered energy of simulated pulses.

During this project year, we utilized this toolbox to explore sparse representations of PMT output signals. Traditional dictionary-learning methods were unsuccessful, and we instead investigated Haar Wavelets. Our experiment consisted of: 1) PMT output signal generation, 2) Haar Wavelet coefficient extraction, 3) lossy signal reconstruction using the largest-magnitude coefficients, and 4) PSD and determination of the start location and delivered energy of the reconstructed signal. We discovered that a small number of coefficients contained the majority of the useful information. For example, at SNR=20 dB, 640-MHz sample rate, and 100-ns acquisition duration (64 samples), the performance in step 4 when we used the largest 16 of 64 coefficients for pulse reconstruction was essentially the same as when we used all coefficients.

Having demonstrated the highly compressible nature of PMT signals, we altered our experiment for the standard compressive-sensing (CS) framework. Step 2 became the process of taking multiple incoherent signal measurements via correlation with Gaussian noise, Bernoulli trial or deterministic Noiselet signals. Step 3 became 3a) solving an L1 optimization problem to find a sparse representation of the signal in the Haar Wavelet domain given these incoherent measurements and 3b) reconstructing the signal from the estimated Haar Wavelet coefficients. We determined that only four incoherent measurements were required to achieve reasonable PSD for simulated conditions of SNR=17 dB, 200-MHz sample rate, and 160-ns acquisition duration (32 samples).

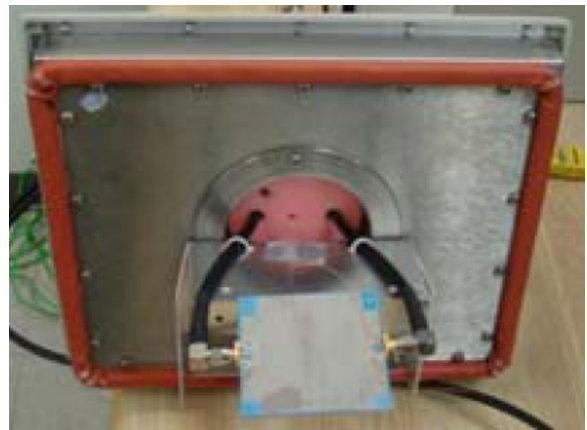
NUCLEAR WEAPONS INVESTMENT AREA

From fundamental studies into novel material combinations underlying better sensors and actuators, to more immediately employable sensors for monitoring the environment of weapon components, to improved nuclear weapons communications architectures, the projects in this investment area all aim to provide better, more reliable methods of stockpile stewardship, with potential impacts to related mission areas (such as advanced battery construction and the role of the hydrogen economy in non-fossil-fuel energy generation).

Localized Temperature Stable Dielectrics for Low-Temperature Co-Fired Ceramic Project 148900

This project has addressed bandwidth limitations in low-temperature co-fired ceramic (LTCC) technology, a multilayer 3D packaging, interconnection and integration microsystem technology found extensively in wireless communication devices ranging from radio (RF) to microwave (MW) frequencies. A major limitation derives from the parameter, temperature coefficient of resonant frequency (T_f), whose optimal value should be zero or as close to zero as possible. However, all current commercial LTCC systems have a T_f in the range $-50 \sim -80$ ppm/ $^{\circ}\text{C}$. To this point in time, efforts to develop 0 T_f LTCC system, including conductors and other embedded materials that are compatible with 0 T_f base LTCC dielectrics, have not been successful.

This project took the approach of establishing localized 0 T_f structures in the most widely used LTCC systems by developing novel compensating materials and incorporating the compensating material locally to LTCC structures where the resonant functions reside. The key materials science challenges included synthesis of appropriate T_f compensating materials and tailoring their compatibility — both physical and chemical — to the existing LTCC system. The results are expected to help Sandia's internal customers with fabrication of temperature-stable multilayer ceramic components and subsystem subsystems for mission-critical applications, as well as to enable broad industrial application in wireless communication using radio and microwave frequencies.



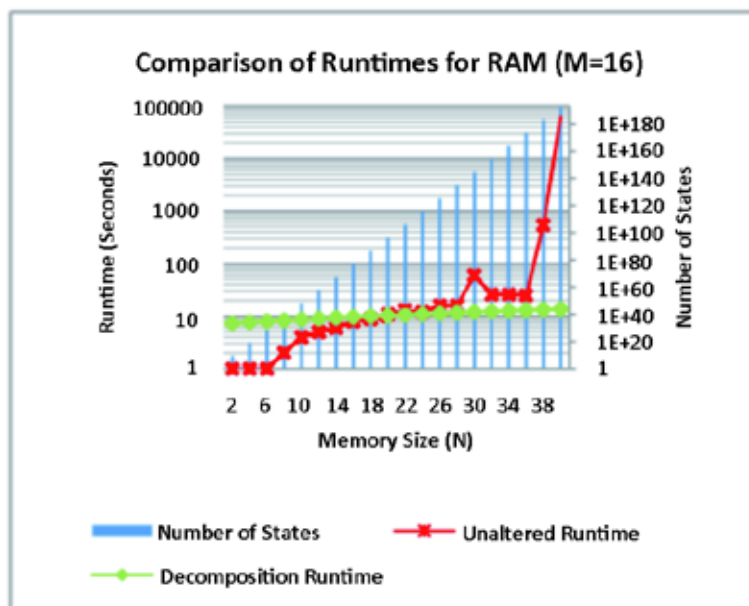
Modified LTCC ready for thermal processing

Exploring Formal Verification Methodology for FPGA-Based Digital Systems Project 154691

A fundamental question for Sandia high-consequence electronics involves the reliability of field programmable gate array (FPGA)-based control systems. Many critical-system electronic components are being replaced by modern digital devices, thus dramatically increasing system complexity. Such systems include those used in aerospace applications, as well as those upgraded as part of nuclear weapons life-extension programs, and the updated designs commonly rely on FPGAs to implement sophisticated logic. A key outcome of this trend is the need to validate the performance of such digital systems to the greatest extent possible.

Ubiquitous in modern hardware, FPGAs are electronic components that are somewhat akin to a tabula rasa, a blank page. Perhaps a more appropriate analogy would be a child's play tool for improving reading—a magnetic slate filled with movable words that the child can reconfigure into a variety of meaningful sentences. In FPGAs, the words are logic blocks that can be connected together in a variety of configurations determined by a user who is addressing specific hardware design requirements. Based upon tools provided by the vendor, FPGAs are thus designed to be configured by a customer after manufacturing, that is, after their logic functional blocks are implemented. One advantage of FPGAs over custom hardware is that they are harder to attack because the design for a processing functionality is not pre-loaded onto a device. Among their other uses, FPGA characteristics make them suitable for implementing cryptographic applications. However, while they offer this attack resistance and flexibility, they can also comprise yet another source of problematic issues, in that, in using the vendor's tools to configure them, a hardware engineer may introduce unintended vulnerabilities.

Noting that there were critical systems at Sandia caught in this limbo, whereby simulation was the primary tool being employed for verification, even while other validation and verification methodologies were beginning to enter the broader realm of FPGA-based system analysis, this project has been adopting and modifying other methods for verification of Sandia critical systems. These include formal verification and decomposition.



Comparison of runtimes for model checking of increasing RAM sizes, run as a single large problem (red) and as a set of decomposed problems (green). As the state space explodes with a problem of larger sizes, the runtime becomes prohibitive, but remains relatively stable for the decomposed problem

Nuclear Weapons Investment Area

Mesoscale Highly Elastic Structures (MESHERS) for Surety Mechanisms 141689

Year 3 of 3

Principal Investigator: B. H. Jared

Project Purpose:

The purpose of this project is to investigate a new approach to mesoscale elastic elements that meet advanced requirements for surety mechanisms. Current coil-wound wire springs have high variability due to material and process variations forcing mechanism parts to be significantly overdesigned, antithetical to design goals requiring reduced mass and improved response time. Mesoscale highly elastic structures (MESHERS) are being developed that yield repeatable spring response with lower component uncertainties. Required research includes investigations of material science and direct machining processes at the mesoscale and the ability to accurately predict performance of complex, 3D, highly elastic structures including material response and surface effects from the fabrication processes. Important research includes the material properties of small features where assumptions of homogeneity break down. This breakdown is especially important for highly elastic members but will apply to small features in weapons components and to small mechanisms in general. Process research quantifies the surface effects of several machining processes and evaluates their modification of material behavior in mesoscale structures. Design development integrates material and process understanding into an integrated design capability, including strategies for creating spring-like response from fundamentally different structures. The resulting structures will exhibit significantly higher repeatability than wire-wound springs and will significantly open the design space to new materials, new geometry, and added capabilities. The results will be applicable to all surety mechanisms and will also have application to small mechanisms in general.

Summary of Accomplishments:

Project milestones were achieved as prototype MESHERS geometries were designed, fabricated and tested in helical and planar forms. Design tools were developed to optimize spring performance within constraints relative to size, stiffness, operating stress, and manufacturability at the mesoscale. Prototype springs have demonstrated low part-to-part variability (5%) and predictable performance (5% model-to-part deviation). Fatigue life of 10^3 to 10^6 cycles has been observed for as-machined springs. Electropolishing research has investigated processes for polishing high aspect ratio features in 304L as fatigue life improvements of 10x have been observed. Degradation of spring performance due to surface effects and/or grain size scales has not been observed as spring responses have maintained correlation to bulk material assumptions and models.

Significance:

Sandia's primary mission to maintain nuclear weapon (NW) surety in the face of evolving threats requires continued development of sophisticated surety strategies. Many of these strategies require decreases in volume and mass of mechanisms to add capability within space constraints. A further constraint to these strategies is the continual desire for improving mechanism quantification of margin and uncertainty (QMU) either through improved design or reduced process uncertainties. MESHERS addresses each of these fundamental needs through the development of smaller highly elastic structures with improved reliability, uncertainty and performance that will support arming, fusing, and firing (AF&F) developments, a core Sandia product.

Refereed Communications:

L.M. Serna, B.L. Boyce, B.H. Jared, and G.A. Knorovsky, “Effect of Electropolishing on the Surface Topography of Micro-Wire Electrodischarge Machined Simulated Coil Gaps,” in *Proceedings of International Conference on Micromanufacturing*, 2012.

B.H. Jared, B.L. Boyce, G.A. Knorovsky, and L.M. Serna, “Design and Direct Machining of Mesoscale Elastic Structure,” in *Proceedings of International Conference on Micromanufacturing*, 2012.

Selective Stress-Based Microcantilever Sensors for Enhanced Surveillance

141691

Year 3 of 3

Principal Investigator: M. D. Allendorf

Project Purpose:

Assessment of component aging and degradation in weapon systems remains a considerable challenge for the Integrated Stockpile Evaluation program. Analysis of weapon atmospheres can provide degradation signatures and indicate the presence of corrosive vapors. However, a critical need exists for compatible in situ sensors to detect moisture and other gases over stockpile lifetimes. This inhibits development of both “self-aware weapons” and fully instrumented weapon test platforms that could provide in situ data to validate high-fidelity models for gases within weapons. We are developing a platform for on-demand weapon atmosphere surveillance based on static microcantilevers (SMC) coated with nanoporous metal organic frameworks (MOFs) to provide selectivity. SMCs detect analytes via adsorbate-induced stress and are up to 100x more sensitive than resonant beam designs. They are also low-power, highly compact devices that can be manufactured using complementary metal oxide semiconductor (CMOS) technologies. MOFs have ultrahigh surface areas (up to 6000 m²/g), are extremely radiation resistant, and have a hybrid inorganic-organic structure providing much more flexibility to tailor pores for selective adsorption than any other nanoporous material. We are creating MOF-based recognition chemistries for H₂O, CH₄, O₂, and other gases using validated atomistic modeling tools to guide synthesis. A stress-based hydrogen detection capability using a NiPd coating is also being tested. MOFs exhibiting large adsorbate-induced structural deformations are being used to maximize sensitivity by creating large interfacial stresses. Novel cantilever designs incorporating reference cantilevers and integrated temperature measurement for in-situ self-calibration are being fabricated. Sensors operating in either dosimeter or real-time mode are being developed. Finally, using simulated weapon atmospheres, long-term device performance (drift, calibration, noise, and cross sensitivity) is being quantified. The project leverages the Center for Integrated Nanotechnologies (CINT) microcantilever discovery platform, Microsystems and Engineering Sciences and Applications (MESA), and an ongoing collaboration with Georgia Institute of Technology (Georgia Tech) School of Mechanical Engineering to develop static microcantilever (SMC) devices, fabrication methods, and data collection strategies.

Summary of Accomplishments:

Key accomplishments in FY 2012 are as follows:

- We demonstrated continuous operation of a humidity sensor capable of detecting concentrations as low as 280 ppb (–85 °C frost point). The sensor has been in continuous operation for more than 10 months. This device performs as well as state-of-the-art humidity sensors on the market but is very compact and requires very low power (~100 μW).
- We showed that a wide range of hydrocarbons can be detected using MOF coatings to functionalize sensors, including typical solvents such as alcohols, acetone, and chlorinated species, and that this can be done selectively.
- We developed extensive expertise in growing MOF thin films on a variety of sensing devices. We can now deposit nine different materials representing several major subcategories of these materials. Multilayer coatings can also be grown, which allows us to design sensors blind to common interferents such as water vapor.
- We completely redesigned the original microcantilever platform used in the project, in collaboration with a research group in Mechanical Engineering at Georgia Tech. The new device is mechanically

more robust and has an on-board reference for stable operation as well as in situ temperature measurement.

- We collaborated with faculty and students at Georgia Tech to develop new capabilities for computational screening of MOFs, which now allows us to design materials for specific sensing purposes.
- 5 journal articles were published, with three more manuscripts under way.
- One patent was issued and another patent application was submitted.
- 5 conference presentations were given (1 invited).

Significance:

The availability of a suite of effective environmental chemistry sensor technologies is highly desirable because a variety of Sandia needs already exist. This project targets two NNSA-specific stockpile transformation needs: state-of-health prediction and routine deployment in the emerging component surveillance program. A third obvious application is for emerging DHS-related real-time chemical detection schemes (e.g., chemical intrusion threats). Finally, the new science and engineering developed here demonstrates for the first time that the rapidly expanding class of nanoporous materials known as metal-organic frameworks can be integrated with microelectromechanical system (MEMS) devices to create gas sensors that compete with state-of-the-art sensors.

Refereed Communications:

V. Stavila, J. Volponi, A.M. Katzenmeyer, M.C. Dixon, and M.D. Allendorf, “Kinetics and Mechanism of Metal-Organic Framework Thin Film Growth: Systematic Investigation of HKUST-1 Deposition on QCM Electrodes,” *Chemical Science*, vol. 3, pp. 1531-1540, February 2012.

L.E. Kreno, K. Leong, O.K. Farha, M.D. Allendorf, R.P. Van Duyne, and J.T. Hupp, “Metal-Organic Framework Materials as Chemical Sensors,” *Chemical Reviews*, vol. 112, pp. 1105-1125, November 2011.

A.L. Robinson, V. Stavila, M.I. White, S.M. Thornberg, T.R. Zeitler, J.A. Greathouse, and M.D. Allendorf, “Ultra-Sensitive Humidity Detection Using MOF-Coated Microsensors,” *Analytic Chemistry*, vol. 84, pp. 7043-7051, August 2012.

A. Venkatasubramanian, J.-H. Lee, V. Stavila, A.L. Robinson, M.D. Allendorf, and P.J. Hesketh, “MOF @ MEMS: Design Optimization for High Sensitivity Chemical Detection,” *Sensors and Actuators B*, vol. 168, pp. 256-262, June 2012.

T.R. Zeitler, M.D. Allendorf, and J.A. Greathouse, “Grand Canonical Monte Carlo Simulation of Low-Pressure Methane Adsorption in Nanoporous Framework Materials for Sensing Applications,” *Journal of Physical Chemistry C*, vol. 116, pp. 3492-3502, December 2011.

The Role of Hydrogen Isotopes in Deformation and Fracture of Aluminum Alloys 141692

Year 3 of 3

Principal Investigator: C. W. San Marchi

Project Purpose:

Tritium reservoirs for gas transfer systems are high-energy-rate forged austenitic stainless steel. The forging process is designed to control strength, grain size, dislocation microstructure, and forging flow lines. Commercial operations do not attempt to simultaneously satisfy all of these materials variables in forged product, making it difficult to source forgings from the commercial sector. Aluminum alloys represent a potential alternative to forged stainless steel for tritium containment with several important advantages. Structural aluminum alloys can be strengthened by precipitation, eliminating the need for forging. In addition, aluminum alloys have very low solubility of hydrogen, which may explain the perception that they are immune to gaseous hydrogen. Due in part to the difficulties of observing hydrogen in metals and executing tests in high-pressure gaseous hydrogen, the scientific foundation for establishing immunity of aluminum to hydrogen-assisted fracture has not been adequately demonstrated in the literature. Hydrogen transport within the metal must precede hydrogen-assisted fracture, and this limiting condition appears impossible to quantify in conventional testing. This project seeks to clarify the surface kinetics of hydrogen uptake and transport in aluminum alloys during exposure to gaseous hydrogen and to determine the structural compatibility of aluminum in high-pressure gaseous hydrogen. We have employed advanced characterization techniques to enhance the understanding of the thermodynamics and kinetics of both hydrogen on the surfaces of aluminum alloys and hydrogen transport in the bulk. Knowledge of these physics will be coupled with testing in the high-pressure hydrogen laboratory with the aim of establishing methods for determining conservative engineering properties appropriate for the design of aluminum vessels for the containment of high-pressure gaseous hydrogen and hydrogen isotopes. Unique facilities exist at Sandia, California, which are necessary to illuminate the fundamental physics of hydrogen-aluminum interactions (including low energy ion scattering and thermal desorption spectroscopy, as well as mechanical testing in gaseous hydrogen at high pressures).

Summary of Accomplishments:

We used low energy ion scattering (LEIS) and direct recoil spectroscopy (DRS) to examine hydrogen binding to Al surfaces, developing appropriate techniques to crystallographically map aluminum surfaces. We considered Al surfaces dosed with atomic H. Our time-of-flight spectroscopy measurements confirm that only a low coverage of hydrogen could be adsorbed at room temperature. We were not able to discern structure within the adsorbed H on a flat Al(111) surface, suggesting that hydrogen does not strongly bind to the Al(111) surface. In contrast, analysis of the stepped Al(332) surface shows preferential binding to the step edges, demonstrating that surface defects are important binding sites for the aluminum-hydrogen system.

We have shown that dislocations and Mg can serve as potent traps. Alloys with significant Mg content should probably be avoided in hydrogen environments. We are also able to measure evidence of trapping to microstructural features that have smaller trap occupancy in typical systems (vacancies and grain boundaries). Because microstructural changes in Al (particularly precipitate dissolution and coarsening) can be substantial over the temperature range used in total dissolved solids (TDS) analysis and because many peak energies seem to be similar, a more systematic study of trapping over model materials with systematically varied compositions and microstructures and using alternative techniques will be needed to better inform the behavior of the engineering alloys that are of interest.

We have mechanically tested a number of aluminum alloys in high-pressure gaseous hydrogen. Results of this testing show that the fracture and fatigue properties of engineering aluminum alloys are not significantly changed by gaseous hydrogen. The fatigue testing in particular was used to probe the long-term exposure of aluminum to hydrogen in the presence of an active defect, and it was shown the fatigue crack growth was not accelerated by hydrogen in stark contrast to steels.

Significance:

New structural materials must be identified for tritium compatibility in nuclear weapons (NW) applications; aluminum is the obvious candidate for improving manufacturability and long-term reliability for tritium service. Aluminum is also an important structural material in the context of establishing energy security; aluminum represents a desirable alternative to the expensive materials that are currently used in hydrogen fuel cell applications. This project provides the first scientific stages of validating the hydrogen compatibility of aluminum, which informs tritium compatibility studies planned for the future.

Refereed Communications:

R.D. Kolasinski, R.A. Karnesky, and C. San Marchi, “Interactions between Gaseous Hydrogen and Aluminum Alloys,” in *Proceedings of the 2012 International Hydrogen Conference*, 2012.

Localized Temperature Stable Dielectrics for Low Temperature Co-Fired Ceramic 148900

Year 3 of 3

Principal Investigator: S. X. Dai

Project Purpose:

Low temperature co-fired ceramic (LTCC) is a multilayer 3D packaging, interconnection and integration technology. In the past 10-15 years the biggest growth of LTCC technology occurred in wireless communications ranging from radio (RF) to microwave (MW) frequencies. The three key material parameters most important to this application space include dielectric constant, quality factor Q (inverse of dielectric loss), and temperature coefficient of resonant frequency (T_f). For RF/MW circuits incorporating resonator functions, it is highly desirable to have a zero or near-zero T_f ($0T_f$) to fully utilize the communication bandwidth and achieve temperature stability of devices. However, all current commercial LTCC systems have a T_f in the range $-50 \sim -80$ ppm/°C. There were several successful attempts to formulate $0T_f$ LTCC base dielectrics, but so far the efforts to develop $0T_f$ LTCC system, including conductors and other embedded materials that are compatible with $0T_f$ base LTCC dielectrics, have not been successful.

Instead of developing an entirely new $0T_f$ LTCC system, our approach is to establish localized $0T_f$ structure in most widely used LTCC systems to take advantage of existing LTCC technologies and infrastructure. We will explore a method to achieve $0T_f$ by: 1) developing novel compensating materials which have opposite T_f to that of the LTCC base dielectric and 2) incorporating the compensating material locally to LTCC structures where the resonant functions reside. The key materials science challenges include synthesis of T_f compensating materials and tailoring of their compatibility, both physical and chemical, to the existing LTCC system. Our objective is to examine the concept of localized temperature stability for advanced RF/MW applications by addressing related materials science and engineering issues.

Summary of Accomplishments:

We have formulated T_f compensating dielectric materials that possess a T_f opposite to that of existing LTCC dielectrics. The dielectric properties and chemistry of the compensating materials were studied in detail using a variety of electrical and microstructural characterization tools. The co-fireability with a commercial DuPont 951 LTCC was confirmed by closely matched dilatometer shrinkage curves and minimal interfacial reactions. The effect on T_f compensation was analyzed in terms of composition, thickness and placement of the compensating materials. It was found that a higher content of SrTiO_3 in formulation and thicker compensating materials resulted in better T_f adjustment. More importantly, the compensating materials needed to be printed next to the stripline resonators for effective T_f compensation. T_f adjustment is negligible when the compensating materials were printed one or two LTCC layers away from the resonator lines. The phenomenon was explained by a disproportionally high electromagnetic energy concentration to the compensating materials through total internal reflection of electromagnetic (EM) field when the compensating layer with high dielectric constant is placed next to a resonator line.

The effective dielectric constant of the composite multilayer LTCC structure incorporating T_f compensating materials was calculated from the transverse transmission line admittance. Resonant frequency was then simulated by method of momentum to capture the temperature dependence of the resonant frequency of the stripline resonator. The simulated results of T_f compensation agreed well with experimental findings.

We have also demonstrated that the T_f of a 1.9-GHz S-band filter fabricated in LTCC can be reduced from the original ~ -70 ppm/ $^{\circ}\text{C}$ to nearly 0 ppm/ $^{\circ}\text{C}$ when a SrTiO_3 -based T_f compensating material is co-fired next to the filter lines.

Significance:

We have developed a novel method to achieve localized temperature stability in a commercial multilayer LTCC. The critical development is the synthesis and understanding of T_f -compensating materials that are co-fireable with LTCC. The outcome of this project provided a science-based engineering solution to realize temperature stability in a widely adopted LTCC system. The results are expected to potentially help Sandia's internal customers with fabrication of temperature-stable multilayer ceramic components and subsystems for mission-critical applications, as well as to enable broad industrial application in wireless communication using radio and microwave frequencies.

Refereed Communications:

S. Dai, "Localized Temperature Stability in a Multilayer LTCC Package," in *Proceedings of the 44th International Symposium on Microelectronics*, pp. 539-543, 2012.

S. Dai and L.-H. Hsieh, "Effective Compensation of the Temperature Coefficient of Resonant Frequency in LTCC," in *Proceedings of the Ceramic Interconnect and Ceramic Microsystems Technologies*, pp. 627-633, 2012.

S. Dai, "Localized Temperature Stability in Multilayer LTCC," *Journal of Microelectronics and Electronic Packaging*, vol. 8, pp. 1-6, 2011.

Development of Ab Initio Techniques Critical for Future Science-Based Explosives R&D

151351

Year 2 of 3

Principal Investigator: R. R. Wixom

Project Purpose:

Density functional theory (DFT) has emerged as an indispensable tool in materials research since it can accurately predict properties of a wide variety of materials at both equilibrium and extreme conditions. However, for organic molecular crystal explosives, successful application of DFT has largely failed due to the inability of current exchange-correlation functionals to correctly describe intermolecular van der Waals' (vdWs) forces. Intermolecular vdWs forces are critical to predicting chemistry and physics of explosives at both equilibrium and under stimuli. For the explosive pentaerythritol tetranitrate (PETN), vdWs interactions may dominate the physics for isotropic pressures up to 10 GPa, which implies that we cannot accurately apply DFT for investigating aging, safety, or the margins associated with initiation of PETN or any high explosive. This is unfortunate since explosives research is extremely difficult, expensive, and dangerous while at the same time essential to DOE/NNSA core missions.

We are constructing a completely new functional using the subsystem functional scheme that was recently used to successfully include correct surface treatment into the AM05 functional (published by Armiento and Mattsson, 2005). Despite decades of research, resulting in hundreds of approximate functionals, no functional treating both vdWs and stronger bonds with equal accuracy is available. Even though the vdWs problem can be circumvented by performing DFT-AM05 calculations only at very high pressure, successful investigations at equilibrium and low compression (weak shock), where vdWs forces dominate, will require a new functional provided by a more sophisticated approach such as the subsystem functional scheme. This new functional will provide an accurate first-principles link to the ongoing mesoscale and continuum physics efforts to model explosive components and additionally will have broad dramatic impact across many fields of science including energy, biology, pharmaceuticals, and the study of any weakly bonded materials systems such as polymers and those applications involving graphene.

Metal-Insulator-Transition-Based Limiters

151352

Year 2 of 3

Principal Investigator: C. Nordquist

Project Purpose:

The purpose of this project is to explore novel materials and devices for next-generation limiters. Limiters are essential for protecting receivers since they pass low-level signals but block high-power signals that could damage sensitive electronics. Existing limiters using semiconductor diodes are generally restricted by capacitance that forces undesirable compromises among bandwidth, power handling, sensitivity, and survivability. Novel materials and devices provide potential for improved bandwidth, insertion loss, and power handling.

Metal-insulator transition materials (M-ITM) offer the potential for revolutionary improvement of limiters. Two material classes with the potential for high-power broadband power limiting are metal oxides and chalcogenides, both of which exhibit thousand-fold changes in resistance at a specific transition temperature. Microwave heating or electronic transitions at high power can trigger this M-ITM and create a reversible short circuit, reflecting undesired energy away from the receiver. Because the limiting mechanism is purely resistive, these materials may enable broadband, low-loss, high-power limiters with a small footprint when compared with conventional limiters.

This project is investigating M-ITM for improved systems and applying these materials to a prototype demonstration device. We are investigating material fundamentals with a goal of tailoring the transition temperature, increasing the resistance ratio, and developing integration approaches. A device thrust motivates the materials requirements and will apply the materials to demonstrate limiters, test the limiters under continuous and pulsed power, and provide feedback for further materials development.

This research is important because M-ITM for these applications are currently at TRL2 with few demonstrations of functionality to date. No reports of critical parameters exist; unknowns include power handling, transient behavior, and recovery time. If this project is successful, it will establish a technology foundation that will improve future receivers and systems.

Thermoelectric Materials: Mechanistic Basis for Predictive Aging Models and Materials Design

151353

Year 2 of 3

Principal Investigator: D. L. Medlin

Project Purpose:

New thermoelectric devices are being developed for use as power sources. These devices rely on thermoelectric materials based on alloys of Bi_2Te_3 to perform the active function of converting heat flow to electrical power. Regardless of the final design and the specific heat source, the long-term performance of these devices ultimately rests on the properties of the thermoelectric materials. Understanding the aging mechanisms of the relevant Bi_2Te_3 -based materials (including changes in the material and its interaction with contact materials) is critical if we are to confidently predict and support the 15-30 year performance of these devices. Looking forward, we also recognize that advances in nanoscience and control of electronic structure are yielding unprecedented improvements in thermoelectric materials technology—advances that are now extending to bulk Bi_2Te_3 -based materials in the temperature ranges relevant for stockpile application. A fundamental understanding of the interplay between performance and stability will be critical in developing new materials that take advantage of these recent advances while maintaining the reliability required for adoption into the future stockpile. To provide this understanding, we are pursuing a comprehensive program of experiment and materials theory and modeling. Our goal is to discover and quantify the mechanisms governing the performance and long-term behavior of Bi_2Te_3 -based thermoelectric materials and to integrate these findings into a predictive science framework. To reach this goal, we will draw on advanced tools for microscopy and transport analysis, and we will advance the state-of-the-art in modeling both materials stability and thermoelectric properties. This capability and knowledge base will be important in future years in meeting our long term responsibility for the new Bi_2Te_3 -based thermoelectric power systems currently being developed and in guiding the engineering of more advanced thermoelectric materials for improved reliability and tailored thermal response specific to application needs.

Software-Defined Telemetry using a Programmable Fuzing Radar 151354

Year 2 of 3

Principal Investigator: D. Young

Project Purpose:

Weapon radars and joint test assembly (JTA) telemetry transmitters are traditionally implemented in separate hardware even though both use roughly the same frequency band. Recent advances in high-speed digital-to-analog converters (DAC) enable the direct digital synthesis of radio-frequency (RF) signals without intermediate analog processing. Similarly, high-speed analog-to-digital converters (ADC) allow direct conversion of an RF signal to digital baseband. Incorporating these high-speed parts enables increased flexibility in design and opens exciting possibilities for combining telemetry functionality into radar hardware with only software (firmware) changes.

Combining radar and telemetry would yield higher fidelity test results—there would be no difference in the RF chain between war reserve (WR) and JTA configurations, and some physical modification to the weapon could be avoided. Cost savings from reduced hardware and development time may also be realized.

The direct synthesis and direct sampling architectures we are pursuing are significantly different from current radar and telemetry architectures. Engineering research is required to develop signal-processing algorithms for the simultaneous transmission of both signals and the reception of the radar return signal. Because the telemetry signal interferes with the radar return, significant work is required to isolate the signals. Existing systems use large RF components to achieve this isolation, but we plan to develop digital signal-processing techniques that yield equivalent or better results. Jam resistance will be considered as part of the development. Computer simulation and laboratory testing will be used to develop and then improve the designs.

Nondestructive Gas-Pressure Measurements in Neutron Tubes and Generators 151355

Year 2 of 3

Principal Investigator: R. S. Goeke

Project Purpose:

Neutron generators are a key limited-life component in nuclear weapons and other applications requiring a neutron source to probe or activate a material for analysis. At the heart of the neutron generator is a high-voltage vacuum tube, which contains tritium hydride. The decay of tritium into helium results in a deterioration of the vacuum level, which ultimately results in the end of the neutron generator life. Measuring the pressure inside the tube is a difficult proposition that typically requires destructive analysis. At high pressures, a leakage current can be measured, and some pressure information can also be determined during operation of the ion source. Periodically puncturing sample tubes on the shelf is another way to infer the pressure in a population of tubes. We are pursuing the development of a nondestructive, nonintrusive method by which the pressure inside a neutron generator can be characterized without operating the neutron tube. An accurate measurement of the pressure over a large range of vacuum from 10^{-9} to 10^{-1} Torr is desirable but has not been possible. We plan to solve this challenge by treating the existing vacuum envelope as a Penning- or Redhead-style ion gauge. By creating optimized cross-electrical and external magnetic fields on the existing tube design, we can enhance the electron ionization path and generate a measureable signal into the high vacuum regime. This capability is also needed for vacuum switch tubes such as Sprytrons used in nuclear weapons (NW) firing sets.

While the concept of treating a neutron tube or switch tube as an ion gauge sounds simple, the materials, geometry, and small volumes have prevented previous attempts to measure high vacuum levels. We hope to overcome this by modeling and optimizing the fields for our test system. Characterization of emission fields and ionization thresholds for existing tube geometries should allow us to succeed when this was not previously possible.

All-Optical-Fiber Architecture for Direct Optical Ignition 151356

Year 2 of 3

Principal Investigator: S. E. Bisson

Project Purpose:

Optical initiation has long been recognized as an attractive alternative to conventional explosives initiation techniques, offering enhanced safety from unintended initiation by external electrical and/or optical energy sources. Current optical initiation concepts are based on traditional Q-switched bulk solid-state lasers, comprising a bulk optical resonator and numerous other bulk optical components for Q-switching, power splitting, and fiber coupling. While significant progress has been made with this particular approach, complexity is, in general, high; size is also an issue, and alignment sensitivity can be a serious problem. While the detailed requirements may vary depending on the particular device, attributes such as compact size, low weight, low power consumption, and susceptibility to high-g loads are common requirements. To meet these challenging requirements, we are pursuing a radically new design for optical initiation based on an all-fiber passively-Q-switched pulsed light source. This architecture has many potential advantages such as size, simplicity (few components), and alignment insensitivity to shock and high-g environments. This work will focus primarily on technical issues related to the passive Q-switch architecture based on the concept of scaled saturation intensity and is aimed at long-term stockpile needs.

MEMS Photoacoustic Spectroscopy

151357

Year 2 of 3

Principal Investigator: A. Robinson

Project Purpose:

After years in the field, materials in weapons suffer degradation, off-gassing, and chemical changes leading to measurable changes of the chemical atmosphere. Chemicals can be corrosive to electronics and other materials, causing accelerated degradation and reduced time-to-failure. Even benign compounds may indicate known or unknown age-related issues that require action. Obtaining reliable chemical information from sealed environments is difficult at best. Stand-alone embedded chemical sensors are typically limited in specificity and require electrical lines while calibration drift makes data reliability questionable. Along with size, these “Achilles heels” have prevented incorporation of gas sensing.

To address this need, we are developing all-optical mid-IR (infrared) MEMS PAS (microelectromechanical systems – photoacoustic spectroscopy) for safe, in situ monitoring of sealed systems. This novel research seeks to overcome limitations of optical access and insufficient interaction path lengths through the use of ever-improving IR fiber optics, photoacoustic spectroscopy, and exquisitely sensitive MEMS microphones and gas cells. Together, these will enable gas monitoring of enclosed areas, including safety exclusion regions. Meanwhile, data collection can be performed by highly powerful standard analytical hardware at a safe standoff distance, allowing equipment to be sufficiently complex and sophisticated to perform high quality calibrations, measurements, and analyses.

Developing all-optical MEMS PAS presents many challenges and risks and requires several disciplines for success. Combining the required elements of this project has never been performed, as few applications have such rigorous requirements for safety and access to accept the risk associated with this challenge. Success will create significant advances toward a small, yet robust all-optical method for in situ characterization of gas composition in war reserve (WR), accelerated aging, and shelf-life units. This has the potential to enhance reliability of the stockpile through 100% gas surveillance and to provide a better understanding of normal gas evolution in systems and subassemblies. Anomaly detection will be possible without adding new sensors. Data will improve estimates of margins and uncertainties.

AF&F Fail-Safe Feature for Abnormal Thermal Environments using Shape-Memory Alloys

151358

Year 2 of 3

Principal Investigator: D. F. Susan

Project Purpose:

This project will increase nuclear safety, security, and performance margins for nuclear weapon Life Extension Programs by creating arming, fusing and firing (AF&F) fail-safe devices that are activated by abnormal thermal environments. This represents a revolutionary advancement in nuclear safety architectures through the development of high-temperature shape-memory alloys (HTSMAs) as mechanical safeing devices. SMAs are metal alloys that can be mechanically deformed into complex shapes at low temperature and then, through heating, can “remember” the original trained shape. Commercial SMAs consist of alloys of nickel/titanium (Nitinol) that are application-limited due to a maximum shape-change temperature of about 100 °C, a temperature too low to be useful in abnormal thermal environments due to overlap with normal environments and production processing temperatures. We will develop HTSMAs that have shape-transition temperatures of >180 °C by alloying nickel and titanium with platinum, palladium, or hafnium. Current thermal fail-safe devices operate solely on the principle of inoperability and are performance-limited based on a number of known soft spots. Our approach will operate on the principles of inoperability and incompatibility whereby the HTSMA will 1) fail irreversibly, 2) fail passively, 3) perform predictably, and 4) operate based on a fundamental “first principles” material response.

This research leverages an emerging materials suite that has recently attracted global attention and represents a research area yet to be developed at Sandia. The work will potentially yield an enormous enhancement in fail-safe device performance. New HTSMAs and prototype devices will be created based on a fundamental, science-based materials investigation in collaboration with NASA’s Glen Research Center. This work is cutting edge and high-risk as HTSMAs have not been well characterized or developed into viable devices due to such factors as cost, precision in alloying composition, and incomplete knowledge of alloy transformation properties. A tremendous amount of fundamental research is required to target alloy compositions, properties, and processing techniques that will yield useful abnormal-temperature fail-safe devices.

New Composite Separator Pellet to Increase Power Density and Reduce Size of Thermal Batteries

151359

Year 2 of 3

Principal Investigator: L. A. Mondy

Project Purpose:

The separators in thermal batteries are produced by the slow, labor-intensive pressing of a magnesium oxide-electrolyte powder blend into pellets. However, one type of magnesium oxide is no longer produced, and despite over 15 years of research, no replacement powder has been found that is capable of holding the electrolyte as well. Concurrently, there is a need to provide more functionality in a limited amount of space, leading to requirements for smaller and lighter batteries. Unfortunately, pressed separator pellets are too brittle if made thin, so battery stack heights are difficult to reduce while maintaining power output. We are pursuing a novel manufacturing process for separators that will lead to significantly smaller battery stacks, improved performance, and decreased production costs; it will provide a much needed replacement for a critical material that is no longer available.

We are developing novel thermal battery separators using self-assembling ceramic particles to form ceramic foams with very high porosity and mechanical strength. The ceramic foam starts as an emulsion, where surface-modified ceramic particles migrate to droplet interfaces forming interconnected struts that remain when the emulsion is dried and sintered. The new emulsion-based process must be engineered to meet the complex materials and compatibility requirements of the battery system including wetting properties, high dimensional stability, pore size and connectivity, and electrical impedance. Other advanced processes to form reticulated ceramics are also being investigated and compared with the emulsion templating. Although similar processes have been shown to form exceptionally strong ceramics, no one has attempted to produce thin sheets needed for thermal battery separators. Once a sheet is formed, individual pellets can be cut, eliminating the labor-intensive pressing step. Despite the challenges, if successful, this process will provide a revolutionary means to increase the power density, improve manufacturability, and reduce the overall size and weight of batteries.

Liquid-Metal Environment Sensing Devices (ESDs)

151361

Year 2 of 3

Principal Investigator: P. C. Galambos

Project Purpose:

The purpose of this project is to create a novel microsystem and technology for environmental sensing (shock, acceleration, integrated acceleration) based on the motion of a liquid metal drop (e.g., Hg or Hg/Tl eutectic) through a micro-channel undergoing acceleration. If the integrated g-load as a function of time matches design conditions, the drop will travel through the channel to a position at which it will close an otherwise isolated electrical contact (act as a switch). The package around the drop is sealed to create an electronic component that has man-safety and non-integrated accelerometer applications as well as the envisioned integrating accelerometer application. Desirable design will result in anodic bonding over platinum electrode to produce sealed channels with feedthrough electrical connections, without the use of epoxy. Computational fluid dynamics software (FLOW3D) is being used to enable redesigns to the device, where required, in order to ensure drop-size precision required for predictable drop motion.

Having begun work on sensors and actuators, we are planning the preparation and submission of a journal article and we anticipate being able to present a TRL3 level prototype by the end of next year that meets the target specifications of the chosen applications.

Novel Failure Analysis Technique for Defect or Precursor Detection 152502

Year 2 of 2

Principal Investigator: J. Beutler

Project Purpose:

The ability to successfully detect and localize defects responsible for failure modes in integrated circuits (ICs) is critical in high-quality, high-reliability production. The novel failure analysis technique (NFAT) has the potential to extend these defect localization and screening techniques to advanced technology nodes. Sandia has been a world leader in developing many advanced Failure Analysis (FA) techniques to detect defects in ICs. However, the effectiveness of present FA techniques is declining as IC complexity increases. Often, electrical signals such as excess leakage current and device functionality help identify a failing device. However, in state-of-the-art ICs, these failure modes can be masked by modes of normal operation by other transistors (100s of millions in advanced technology) on the chip. These normal modes of operation often overwhelm any defect mode. This limits the capability of existing FA techniques.

A crucial FA technology is energetic-beam stimuli as it allows for localization of defects within an IC. Energetic sources such as laser beams are known to selectively enhance “failed” electrical signals of a defect and are the basis of many FA techniques. Coupling NFAT with energetic-beam stimuli has tremendous potential.

Conventional FA tools provide a baseline to discover the effectiveness of NFAT as a stand-alone tool or integrated technology.

Summary of Accomplishments:

ICs were evaluated using NFAT, damaged to varying degrees via accelerated testing, and reevaluated with NFAT to detect changes in behavior. Before and after stress data were also collected using conventional FA tools and techniques such as parametric testing, light emission microscopy (LEM), light-induced voltage alteration (LIVA), and thermally induced voltage alteration (TIVA). In many cases, only a subset of conventional FA techniques revealed an induced change in the IC due to accelerated testing. In each of those cases, NFAT also detected that change. Typically, accelerated damage to an IC was only detectable by testing the IC beyond the devices’ manufacturers’ recommended maximum specifications (something that would not be done in prescreening). However, NFAT was able to successfully detect these anomalies without exceeding these specifications.

Work that couples NFAT with beam-based localization techniques shows that NFAT may more effectively localize defects that conventional techniques do not. Whether this indicates a genuine defect region is not completely determined in this study.

Significance:

Many systems require complex, highly reliable microsystems to ensure success. Successful implementation of NFAT will give these programs a powerful and inexpensive tool to perform quick, cost-effective FA that may not be possible or is more difficult to implement presently.

Imaging and Quantification of Hydrogen-Isotope Trapping in Stainless Steels 152506

Year 2 of 2

Principal Investigator: R. A. Karnesky

Project Purpose:

Hydrogen-isotope transport through embrittlement of pressure vessels ultimately limits component lifetime. Understanding hydrogen interactions with structural materials requires knowing not only equilibrium properties (temperature-dependent lattice solubility, diffusivity, and permeability of hydrogen), but also transient properties. Because it enhances local hydrogen concentration, defect trapping greatly reduces fracture toughness and changes deformation properties. It also makes the apparent diffusivity of hydrogen many orders of magnitude different from the equilibrium lattice diffusivity. However, trapping is typically a weak point in current simulations. Usually, only a single trapping mechanism is assumed while multiple trapping mechanisms operate in real microstructures at temperatures of interest. The experimental characterization of trapping has been limited and has focused on high-strength ferritic steels. Austenitic alloys that are candidate materials and have lower equilibrium permeability values for hydrogen have not been analyzed as thoroughly. While the trapping at large features, including grain boundaries and incoherent particles, has been imaged indirectly, smaller features (e.g., precipitates and solute atoms) have not been studied in detail due to fundamental resolution limitations of most analytical techniques.

The location of hydrogen isotopes is imaged in austenitic stainless steel and model materials using local-electrode atom-probe (LEAP) tomography, and trapping energies are measured by thermal desorption spectroscopy. Hydrogen is found to trap at nitrogen solute atoms. LEAP tomography has sub-nanometer resolution and excellent compositional sensitivity due to pulse counting techniques. Site-specific sample preparation is possible using focused-ion beams, enabling us to detect trapping at low-density features, such as grain boundaries in nickel. These unique capabilities of LEAP tomography make it promising for the study of hydrogen isotopes, but it has not previously been used to image trapping in austenitic stainless steels. The experimental work is compared with first-principles calculations of the binding energy of hydrogen isotopes to solid-solution elements in stainless steels and to coherent precipitate/matrix interfaces.

Summary of Accomplishments:

We have imaged directly, for the first time, hydrogen trapping to individual solute atoms. In 21-6-9 (Ni-Cr-Mn) austenitic stainless steels with varying nitrogen contents, radial distribution functions of our LEAP datasets show short-range ordering of deuterium atoms to nitrogen atoms, with the inter-atomic distance corresponding to the distance between octahedral sites in face-centered-cubic iron. We confirmed the preference of nitrogen and hydrogen isotopes for octahedral sites using first-principles calculations. Our thermal-desorption spectroscopic measurements have shown that a 0.2 eV/atom deuterium trap has increasing occupancy with increasing nitrogen content. However, this energy is twice the binding energy we calculated for nitrogen and hydrogen using first principles with no magnetic effects considered. With magnetic effects considered, nitrogen seems to repel hydrogen. This suggests that the model omits an important contribution, perhaps from vacancies.

Further, we have imaged trapped hydrogen at grain boundaries of both ultra-fine-grained Al-Mg and commercially pure nickel. The amount of solute trapped at the boundaries in nickel seems to depend highly on the nature of the boundary. This may explain the high degree of hydrogen embrittlement observed in as-received nickel that is mitigated by grain boundary engineering.

Significance:

There is no other technique that is currently able to measure hydrogen-isotope segregation at length scales below approximately 100 nm, and we have, for the first time, imaged it at sub-nanometer length scales. This new research methodology can be used to understand and model materials intended for hydrogen environments with greater fidelity, providing benefits for energy (including both fusion and hydrogen storage, transport, power) and security (e.g., gas transfer systems). Further, we have improved the understanding of the specific technical alloys that we studied (nitrogen-containing austenitic stainless steel and nickel).

Refereed Communications:

R. Karnesky, N. Bartelt, N. Teslich, and M. Kumar, “Imaging and Quantification of Hydrogen Isotope Trapping,” in *Proceedings of the International Hydrogen Conference*, 2012.

R. Karnesky, N. Yang, C. San Marchi, T. Topping, Z. Zhang, Y. Li, and E. Lavernia, “Solute Distribution and Mechanical Properties of Ultra-Fine-Grained Al-Mg Alloys,” in *Proceedings of the 13th International Conference on Aluminum Alloys*, 2012.

Developing a Multiscale Test Approach for Characterizing NW Polymer Composites 154058

Year 2 of 2

Principal Investigator: T. Briggs

Project Purpose:

Advanced fiber-reinforced nanocomposites (FRNs) are being seriously considered for Sandia applications due to their potential to enhance mechanical performance and reliability. However, as a result of the multiple constituents comprising FRNs, load distribution, deformation, and subsequent failure mechanisms are unknown. The alignment, adhesion, functionalization, spatial distribution, and aspect ratio of the nanoscale reinforcement fibers are all coupled in an unknown, multifaceted manner yet are vital for structural composite applications. These material aspects affect the material's ability to carry external loads and dissipate energy through fracture processes and introduce a new set of scientific challenges to understand FRN behavior. In order to confidently employ FRNs, the strong dependency of material behavior on the complex collection of material parameters needs to be rigorously studied. To address these issues, we conducted an experimental program to obtain a fundamental understanding of advanced FRNs, which are expected to demonstrate new response behavior for design.

This project combines state-of-the-art material systems consolidated from advanced processing techniques with highly developed fracture characterization methods. The findings have generated a significant increase in the knowledge base of energy-absorbing deformation and fracture processes as a result of the presence of nanoscale reinforcement. The effects of doping a traditional fiber-reinforced composite material system with nanoscale reinforcement on deformation and failure have been investigated.

Summary of Accomplishments:

We discovered carbon nanotubes (CNTs) can be adequately dispersed onto an uncured polymeric composite substrate through an electrospinning technique with adequate process parameters chosen.

We found that the exothermic reaction during the cure is affected by the presence of a secondary polymer substrate acting as the transport medium for the CNTs.

We demonstrated that the glass-transition temperature, storage modulus, and Tan Delta are all measurably different between the baseline carbon-fiber-reinforced plastic (CFRP) and the CNT-enhanced system.

We discovered the Mode I and Mode II fracture strain-energy release rate for the CNT enhanced system is far superior over the baseline CFRP material system. In addition, the fracture morphology showed considerable differences associated with the energy-absorbing mechanisms.

We proved finite element simulations to be useful for gaining insight and explaining the mechanisms associated with the complex fracture process observed during double-cantilever-beam experiments for CNT-enhanced composites.

Significance:

The results of this investigation established the critical relationships that allow enhancement of preimpregnated polymer composites with nanoscale reinforcement that did not exist. This insight and methodology can now be leveraged for this material system and others into the future. The design of structural composite materials requires the optimized use of the constituents to obtain the desired response

behavior. This behavior should be both tailorable and predictable. This effort has lead to improvements in existing composite structures and the creation of new materials for a variety of applications in the national interest.

Refereed Communications:

T.M. Briggs, G. O'Bryan, J.L. Skinner, M.E. LaFord, A.L. Vance, and N.R. Moody, "A Novel Method for Homogenous Dispersion of Multi-Walled Carbon Nanotubes onto Prepreg Composite Materials," in *Proceedings of the SAMPE Tech 2012 Conference and Exposition*, 2012.

Exploring Formal Verification Methodology for FPGA-Based Digital Systems 154691

Year 2 of 2

Principal Investigator: Y. Hu

Project Purpose:

With the Life Extension Programs (LEPs), many nuclear weapon (NW) analog electronic components are being replaced by modern digital devices, increasing system complexities dramatically. Ensuring the reliability, security, and robustness of these upgraded systems is critically important. Custom hardware systems are designed and utilized throughout the NW operations space, from controller devices on the weapons to telemetry systems on Joint Test Assemblies (JTAs). These designs commonly rely on the use of field-programmable gate arrays (FPGAs) to implement sophisticated logic. Effective verification, while increasing confidence, can reduce the overall effort in system debugging and testing.

Traditionally, random simulation has been used to demonstrate the correct functionality of digital systems. This approach is highly dependent on test coverage without guaranteeing that the entire event space is covered. Formal verification, on the other hand, constructs a proof of correctness in the mathematical sense.

Formal verification (FV) has emerged as an accepted alternative approach to traditional validation techniques, such as random simulation and directed testing, for ensuring correctness of hardware designs. While FV has been successful in many applications, such as aircraft navigation systems, cryptography, and medical devices, there has been little work at Sandia in this field for NW-related hardware systems. This research initiated the leveraging of FV for high-consequence systems in the NW arena.

We conducted the development of trusted FPGA-based hardware designs through the use of novel FV algorithms. The algorithms, specifically constructed for the NW mission space, perform domain-specific verification at different phases of FPGA design (synthesis, place and route, programming netlist generation) for high-assurance applications, such as surety and telemetry. The verification algorithms support the analysis of critical digital components, such as memory and transceiver blocks, with mathematical reasoning from automated theorem proving and model checking. Such verification detects race conditions and corner cases at an early stage, eliminating system failure and instability during operation.

Summary of Accomplishments:

We have implemented and published a novel decomposition approach for random-access memory (RAM) to solve the state-explosion problem imposed by model checking. By combining automated theorem proving and model checking, we demonstrated that a RAM of any size can be formally verified. We successfully eliminated the limitation on the size of RAM that can be formally verified. Since RAM is a very important component in many NW designs, this approach provides a practical way to ensure the correctness of RAM.

We have evaluated several proposals for integrating an existing event-driven simulator (Orchestra) with an advanced symbolic model checker (NuSMV) to meet the vision of Sandia's future digital design methodology. The candidates include: 1) implementing basic model checking techniques into Orchestra and 2) generating Orchestra models for various logic blocks and providing an application programming interface (API) to NuSMV's model checker.

We then developed a novel, environment-independent framework for enabling formal verification of development-time embedded system designs with minimal burden to the engineer. In our approach, we

allow developers to integrate our verification framework directly into the user's development environment. This allows a user to conveniently switch back and forth between design and verification, promoting development-phase discovery of design errors without the burden of learning a new development tool or completely rewriting their model in a new language. We illustrated our framework's robustness with an implementation built atop Orchestra – a JAVA-based, timing-accurate simulation engine used in FPGA/application-specific integrated circuit (ASIC) development at Sandia.

Significance:

We have increased awareness of this S&T within Sandia. We have successfully proven the feasibility of integrated formal verification technique by developing a novel decomposition scheme that makes model checking possible on any sized RAM.

We developed an integrated approach to testing, assessing the limitations of simulation while also introducing methodologies for formal verification, that is, the static analysis of all possible system states. This research could enable a new approach to designing digital NW components where formal verification is built into the design process. This would make surety a guarantee along with the functionality of the design.

Refereed Communications:

K. Hulin and Y. Hu, "Maintaining Soundness in Hybrid Verification Approaches for Stateful Models: A Case Study," in *Proceedings of the Argentine School of Micro-Nanoelectronics Technology and Applications*, pp. 52-57, 2012.

A Novel Bi-Functional Conducting-Polymer Sensor Material

154762

Year 2 of 2

Principal Investigator: M. Kane

Project Purpose:

A great deal of interest has developed in recent years in the area of conducting polymers (CP) due to the high levels of electrical conductivity that can be achieved, some comparable to that of metals. Conducting polymers have been thoroughly studied as chemical sensors for their sensitivity to a wide variety of analytes. Unfortunately, most literature data on analyte/conducting polymer interactions are based solely on empirical information. The thermal response of these materials is also not fully understood as it depends not only on the polymer crystallinity and molecular orientation but also on the presence of counter anions or dopants. There is some speculation that de-doping, or at least dopant degradation, occurs at elevated temperatures, but there has never been a distinction between local and homogeneous heating and its effect on conductivity.

This work developed a unique bi-functional sensor that utilizes the change in electrical conductivity of a CP from both chemical and thermal stimuli. This sensor has many potential applications, including some related to the stockpile.

Commercially relevant conducting polymers, such as polyaniline and polypyrrole, were investigated for response to various polar or chlorinating solvents and thermal fluctuations, both applied homogeneously and locally. The effects of environmental factors, such as oxygen and radiation, were also elucidated for calibration of the sensor. The results of this investigation yield a fundamental understanding of the mechanisms for electron transport within conducting polymers as it relates to sensor applications. The interplay of careful dopant selection as well as tailoring of the polymer morphology (e.g., crystallinity) yields a conducting polymer that is both sensitive to changes in chemistry and heat and minimally sensitive to environmental oxidation and irradiation degradation. These carefully tailored materials should prove useful for many DOE applications, including the nuclear weapon (NW) stockpile, that require targeted sensing.

Summary of Accomplishments:

- Density functional theory (DFT) modeling was used to model the bandgap and electron density within the conduction band of several polymer-dopant combinations.
- A process was optimized for the synthesis of polyaniline doped with dodecylbenzene sulfonic acid (PANi-DBSA) that is soluble in common organics, such as toluene and xylene. This is very important as it allows processing of the polymer into a castable film. Standard synthesis procedures yield a practically insoluble powder but higher conductivity. In this case, we sacrifice some level of conductivity for ease of processing.
- Polyaniline was synthesized for use in sensor applications with high conductivity (>1 S/cm) by using an organic-acid dopant that acted both as dopant and emulsifier.
- A custom microfluidics sensor prototype was developed and tested for response to localized heat and chemicals of interest; the sensor shows promising response time (<1 second) and behaviors ($>10\%$ change in conductivity).
- A manuscript was submitted (Synthetic Metals) describing the effects of dopant and oxidant ratios on material conductivity; a model was developed by multiple-regression analysis to predict material conductivity.

- The material properties were correlated with morphology via microscopy and diffraction patterns and with localized electron transport mechanisms by conducting atomic force microscopy.
- An invention disclosure was approved for conversion into a patent application describing a method of scale-up for this material by acoustic mixing, making this work commercially relevant.

Significance:

This new sensor material provides a new potential material for NW applications. This study is also of academic importance as the mechanisms for changes in charge carriers within the conducting polymer for locally applied heat and chemical exposure as compared to long-range (bulk) exposure have been investigated through modeling and experiment. Additionally, new processing methods for conducting polymers are used that can benefit many industries that use this type of material (e.g., photovoltaics, organic light emitting diode [OLEDs], supercapacitors, etc.). An optimal balance of conductivity and ease of processing was obtained through this study as well as a model to predict material conductivity.

Refereed Communications:

M. Kane and K. Krafcik, "Soluble Conducting Polyaniline: A Systematic Study of Factors Influencing Conductivity by Regression Analysis," to be published in *Synthetic Metals*.

Ultrafast Laser Diagnostics to Investigate Initiation Fundamentals in Energetic Materials

154813

Year 2 of 3

Principal Investigator: D. Farrow

Project Purpose:

Currently, the chemistry of shock ignition in energetic materials is poorly understood. Models are purely empirical, and no direct measurement approach for probing of the thermochemical environment within a shocked material currently exists. The shock initiation of energetic materials progresses on picosecond time scales behind the shock wave, and there exists a complex feedback between chemical and mechanical processes (changes in temperature, pressure, and particle velocity) that determine the dominant pathways of ignition chemistry. Sandia currently possesses tools for measuring some mechanical properties during this process but does not have a diagnostic to follow thermochemical evolution during ignition. The extreme temporal and spatial resolution required to monitor the ignition process makes development of appropriate experimental tools a significant technical challenge. In this research, we are exploiting recent developments in femtosecond laser spectroscopy to probe the evolution of temperature and critical chemical species on picosecond timescales in both the gas and solid phase of shock-initiated energetic materials. Using time-resolved Coherent Anti-Stokes Raman Spectroscopy (CARS) and other Raman-based techniques, we are directly measuring the material temperature and chemical-reaction dynamics behind the shockwave. Capturing the relevant physical processes will require us to deliver measurements with both extreme temporal and spatial resolution (picosecond and micrometer scales) in a hostile environment where response to the ultrafast Raman probe is rapidly evolving during the measurement. Time-resolved temperature measurements have never been accomplished in a reacting or inert solid material under shock loading at temperatures and pressures typical of initiation. Time-resolved measurement of chemical composition during initiation of energetic materials would provide information about the performance of energetic materials used in the nuclear weapons (NW) stockpile and enable a transition from empirically based models to physics-based predictive simulation. This project will provide Sandia with an experimental capability that is at the forefront of the science of energetic materials and will address programmatic needs in support of NW.

Ion-Induced Secondary Electron Emission and Vacuum Surface Flashover for High Gradient Ion Beam Accelerators

155409

Year 2 of 3

Principal Investigator: J. S. Howard

Project Purpose:

The purpose of this project is to investigate key knowledge areas critical to the design and advancement of compact, portable, high-gradient ion accelerators, particularly the areas of ion-induced secondary electron emission (SEE) and vacuum surface flashover. Although electron-induced SEE is a relatively established science, ion-induced SEE is complicated by multiple mechanisms and specific beam-target interactions. Moreover, published data are of questionable relevance due to the high level of beam purity and target cleanliness, which are highly unlikely in any production application. The goal of this project is to devise a setup whereby ion-induced SEE data are obtained for actual ion-beam sources impacting production-grade materials. This task requires the development of a novel ion accelerator, which can operate with variable perveance. Regarding vacuum surface flashover, data are readily available for SEE yields and critical flashover fields for materials of simple geometries. However, the field distribution on an insulator surface will affect the surface charge distribution, which in turn affects the flashover strength of that insulator. Hence, flashover studies do not directly translate to insulators with different geometries. Our goal is to devise a test setup by which we can determine critical flashover fields for relevant insulator geometries.

Determination of Reaction-Zone Length in Vapor-Deposited Explosive Films 156704

Year 2 of 3

Principal Investigator: R. Knepper

Project Purpose:

The purpose of this project is to determine reaction-zone lengths in explosive materials by precise manipulation of the confinement conditions. Reaction-zone length is a key parameter in modeling explosive behavior. However, many important explosive materials have very small reaction zones that are extremely difficult to measure using standard techniques. In this project, we pursue a new method for determining reaction-zone length at micrometer to sub-millimeter scales by varying the confinement conditions.

While effectively infinite confinement is known to cause a decrease in the critical thickness and an increase in detonation velocity with increased shock impedance, the thickness of confinement needed to become “infinite” and the magnitude of the effect on detonation velocity and critical thickness are largely unknown. An empirical model will be developed during this research that will not only elucidate this relationship but also provide insight into the structure of the detonation reaction zone by using confinement conditions (thickness, shock impedance) to give an indirect measure of the reaction-zone length.

There has not previously been a reliable method for measuring reaction-zone lengths at sub-millimeter scales. Research will focus on explosive materials that have a critical thickness for detonation less than 200 micrometers, which are likely to have very short reaction zones. Both explosive and confinement layers will be vapor-deposited to provide precise control over layer thicknesses and microstructure. Vapor deposition also promotes intimate contact between the explosive and confinement layers, creating a well-defined model system that can be easily incorporated into mesoscale computer simulations. Vapor deposition readily accommodates various film geometries by using shadow masks during deposition, allowing geometric effects to be studied as well.

Gas Permeation Properties of Graphene Membranes

158183

Year 2 of 3

Principal Investigator: L. Biedermann

Project Purpose:

Separation of hydrogen from helium is of interest to Sandia and other DOE labs. Graphene membranes offer a promising alternative to current membrane technologies since a single monolayer of exfoliated graphene is impermeable to helium at room temperature, yet hydrogen intercalates epitaxial graphene to bind to SiC at elevated temperatures. Furthermore, graphene can be fabricated on a commercial scale and transferred to a variety of substrates.

This project will investigate how gas permeation through graphene may be optimized by careful design and assembly of graphene membranes. Exfoliated graphene, which is the highest quality form of graphene, is impermeable to helium and larger gases at room temperature and can withstand pressure differences up to 600 kPa [Bunch 2008]. Density-functional theory (DFT) simulations confirm that gasses cannot permeate through graphene's benzene rings. However, hydrogen can intercalate epitaxial graphene at 600–1000 °C; grain boundaries and Stone-Wales defects are likely permeation pathways.

Investigation of permeation through chemical-vapor-deposition (CVD)-grown graphene and reduced graphene oxide (RGO) will allow us to determine how intrinsic properties of these graphene sources, such as grain sizes and the presence of defects and grain boundaries, affect the permeability. CVD-graphene and RGO were selected since they are commercially scalable, easily transferrable forms of graphene, unlike exfoliated or epitaxial graphene. To evaluate the utility of graphene as a selective membrane, permeation of various gases and gas mixtures will be measured.

We will develop methods to fabricate high-quality-graphene membranes on porous substrates and will determine under what temperature and pressure conditions graphene is a permeable membrane. Development of an alternative mechanically robust permselective membrane will directly benefit the nuclear weapons (NW) mission.

Chemical Enhancement of Surface Kinetics in Hydrogen Storage Materials 158853

Year 1 of 3

Principal Investigator: D. Robinson

Project Purpose:

In much of the temperature range where palladium alloy powders store hydrogen, the rates of hydrogen uptake and release are limited by chemical reactions at the surface. A stable surface hydride forms that has an undesirably high barrier to transport into the bulk metal or back into the gas phase. To store or release hydrogen more quickly than this allows, engineered systems would require extra storage material or higher pressure drops. Overcoming kinetic limitations could thus improve volume and weight efficiency when fast performance is needed.

We believe that enhanced kinetics can be achieved by destabilizing the surface hydride so that it more closely matches the stability of the bulk hydride. Recent modeling by others predicts that near-surface alloys — submonolayers of alloy elements at or just below the palladium surface — can cause the adsorbed states to be energetically equivalent to the bulk states, facilitating transport of hydrogen between them. We have a new and unique capability, electrochemical atomic layer deposition that allows us to make these surface alloys. We will extend our experience with film substrates, conformally applying layers of alloy elements to gram quantities of micrometer-scale palladium powders. Our hypothesis will be tested through measurement of hydrogen isotope exchange rates. We expect compounded improvements in exchange rates if the surface modification is applied to nanoporous powders that offer faster solid-phase transport.

Our work takes advantage of recent laboratory discoveries in atomic-scale fabrication, develops the new technique into a practical method, and uses it to pursue recent theoretical developments that are not yet practically demonstrated. If the development of this application is successful, we will have solved a longstanding performance problem, enabling a cascade of other improvements in hydrogen-isotope-storage system design that build upon new optimal flow rates and pressures.

Advances in High-Dynamic-Range Resonant Accelerometers

158854

Year 1 of 2

Principal Investigator: R. H. Olsson

Project Purpose:

The project addresses the fundamental challenges of simultaneously achieving the dynamic range and radiation hardness required for nuclear weapons (NW) accelerometers. Capacitively sensed accelerometers are inherently nonlinear because voltage/capacitance is a nonlinear function of proof mass displacement and beam loading results in bending (capacitive) rather than axial strain (resonant). To overcome these inherent nonlinearities, capacitive feedback is used to hold the proof mass in a fixed position. This capacitive feedback force is highly sensitive to dielectric charging induced under radiation, creating enormous, permanent errors in acceleration measurements once exposed to NW radiation environments.

Resonant accelerometers are known to have inherently high dynamic range without force feedback, theoretically >10 million for 1-kHz accelerations, due to mechanical linearity and modulation of frequency as the transduction method. However, the dynamic range of resonant accelerometers is limited at frequencies of interest to NW by phase noise in the readout electronics. Phase noise determines the minimum frequency shift that can be measured and therefore sets the minimum detectable acceleration.

We are pursuing a novel mechanical-chopper stabilization (MCS) approach to increase the signal to noise ratio (SNR), and thus the dynamic range, in resonant accelerometers. In this approach, the accelerometer proof mass is driven to vibrate at high frequencies by a very-low-phase-noise quartz- crystal oscillator. The forced vibration performs a mixing function, translating the acceleration spectrum around a sideband created by the crystal oscillator frequency instead of directly around the sensing-beam's resonant frequency. This shift greatly reduces the phase noise, thus increasing the SNR. This MCS also makes the accelerometer readout insensitive to radiation. While electronic chopper stabilization has been widely applied to mitigate amplifier $1/f$ noise in capacitive accelerometers, electronic chopper stabilization is incompatible with resonant sensing. The research and mechanical implementation will enable application of this valuable technique to higher-dynamic-range resonant sensors.

Impact of Crystallization on Glass-Ceramic-to-Metal Bonding

158855

Year 1 of 3

Principal Investigator: S. X. Dai

Project Purpose:

The purpose of this project is to develop a fundamental materials and process science basis that can subsequently be employed to pursue high performance and reliability glass-ceramic (G-C)-to-metal seals in war-reserve (WR) components.

A robust G-C-to-metal seal must have: 1) a strong chemical bond between G-C and metal and 2) a controlled coefficient-of-thermal-expansion (CTE) match between G-C and metal for long-term structural integrity. Recrystallizable G-Cs have been extensively studied and widely used for such sealing applications because of their controllable CTEs based on process conditions. However, while it is well known that the precipitation of multiple crystalline phases in a recrystallizable G-C substantially changes the chemistry of the residual glass, the effects of residual-glass chemistry on the wetting and bonding at the G-C/metal interface remains largely unexplored.

We are studying the interface between the G-C and the metal and the effects of crystallization in the G-C on the bond strength. The study represents a major step forward from current knowledge on glass-metal seals, which is predicated primarily on controlling the crystallization in the G-C to achieve CTE match to the metal. The goals are to: 1) understand the interfacial reduction-oxidation (redox) process that is essential for strong chemical bonding, 2) investigate the change of glass chemistry resulting from crystallization and its effect on the redox process, and 3) explore paths that enhance the interfacial redox process for improved glass-metal bond.

Synthesis of Wear-Resistant Electrical-Contact Materials by Physical Vapor Deposition

158856

Year 1 of 3

Principal Investigator: S. V. Prasad

Project Purpose:

Electromechanical devices contain electrical contacts to insure passage of signals or power. In addition to providing low and stable contact resistance, materials for electrical contacts should have a low friction coefficient to enable reliable operation at low activation forces, be thermally and chemically stable over extended periods of time, and should have inert surfaces that should not form surface films which compromise the contact resistance. Balancing contact resistance, friction, and other requirements is a highly challenging task, as attempts to decrease the electrical contact resistance typically result in increased friction. Electroplated hard Au, used extensively in electrical contacts, contains minor metal alloying elements (e.g., Co, Ni) for hardening and decreased adhesion and friction. Over prolonged periods of time, these alloying elements (Co or Ni) are known to segregate to the surface, causing uncertainties in the performance and reliability of the electromechanical device. Besides, electroplating is not considered to be an environmentally friendly process. Utilizing modern physical vapor deposition (PVD) technologies, we are currently developing materials with novel architectures that are radically different from the legacy materials. Our main goal is to tailor the electrical contact resistance (ECR) vs. friction in gold films through microstructural control at the nanoscale. On a more fundamental level, the work is also directed at identifying the regimes that will cause grain growth due to combined action of frictional forces and electric current that will make the grain structures unstable. We then use this knowledge to explore novel pathways to suppress this phenomenon. Some of the highlights of this project include the synthesis of novel new surface materials: 1) electron-beam evaporated Au with minute quantities of semi-conducting ceramic particles to pin the grain boundaries and 2) structures comprised of Au-Al₂O₃ nanolaminates by pulsed layer deposition (PLD), where 1-2 nm thick Al₂O₃ layers sandwiched between Au will act as barriers to recrystallization and grain growth. A novel tester has also been designed and built to make simultaneous measurements of friction and ECR during sliding contact in regimes relevant to nuclear weapon component reliability.

Extension of Semiconductor Laser Diodes to New Wavelengths for Novel Applications 158857

Year 1 of 3

Principal Investigator: M. H. Crawford

Project Purpose:

Extension of laser diodes (LDs) to the deep ultraviolet (DUV) is thus far unrealized but would be a major technological breakthrough. Beyond commercial applications, such lasers are of interest for a number of national security applications. Over the past decade, advances in AlGaIn semiconductor alloys have led to the first DUV light-emitting diodes. However, demonstration of DUV LDs has been thwarted by a lack of fundamental insight and solutions to formidable AlGaIn materials science challenges.

Our effort combines Sandia's state-of-the-art AlGaIn growth and fabrication capabilities in Microsystems and Engineering Sciences and Applications (MESA) with advanced modeling to overcome these challenges. Innovative approaches to p-type doping include bandstructure engineering to dramatically reduce acceptor activation energies. Mitigating extended crystalline defects will involve Sandia's recently demonstrated patterned overgrowth process to promote defect annihilation. New insight into non-radiative, atomic-scale defects will be gained using deep-level optical spectroscopy, a technique mastered by few groups worldwide. Sandia-developed laser models will be used to guide AlGaIn bandstructure engineering for maximizing material gain. Finally, LD development will include exploration of a novel laser architecture that has the potential to overcome long-standing challenges in AlGaIn LD design.

Deciphering the Role of Residual Stresses on the Strength of Adhesive Joints 159749

Year 1 of 2

Principal Investigator: J. M. Kropka

Project Purpose:

The reliable operation of many electrical, mechanical, and optical assemblies depends on the integrity of adhesively bonded joints. The strength of an adhesive joint is determined by a number of factors which can include the cohesive strength of the adherent and adhesive materials that make up the joint, the interfacial bonding strength between adherend and adhesive, the presence of residual stresses in the adhesive, and the stress distribution in the joint during mechanical loading. The focus of this work will be on one of these contributing factors, the residual stresses built up in a polymer adhesive during preparation of the joint. The ability to accurately predict the strength of an adhesive joint relies on understanding the role of residual stresses, which has not been fully resolved. A challenge in developing this understanding rests in designing a joint in which residual stresses can be varied without influencing other factors that contribute to the ultimate joint strength.

The napkin-ring (NR) geometry may offer a solution to the challenge of controlling residual stresses without influencing other factors that contribute to joint strength. At relatively small joint aspect ratios (approximately 2-to-1, width-to-thickness), NR residual stresses are insignificant. In addition, the stress profile of the joint during mechanical loading is uniform. Thus, the stress-at-failure for the joint tracks the yield stress of the polymer adhesive. Residual stresses in the adhesive can be changed systematically by decreasing bond thickness (increasing the bond aspect ratio), while the loading stress distribution will remain uniform. Coupled with finite element analysis of the local stress distribution in the joint, tests of NR joint strength as a function of bond aspect ratio and temperature may be able to resolve the influences of residual stresses in the adhesive on both the joint failure load and the mechanism of failure.

Inherent Secure Communication Using Lattice-Based Waveform Design 161862

Year 1 of 3

Principal Investigator: M. O. Pugh

Project Purpose:

The wireless communication channel is susceptible to eavesdropping due to the broadcast nature of the electromagnetic medium. Traditional approaches to combat these insecurities have included encrypting the data via cryptographic methods, hiding the data in the noise floor as in wideband communications, or nulling the signal in the spatial direction of the adversary, using array-processing techniques.

Recent advances in signaling constellation design have shown that an additional level of security exists at the physical layer. By appropriately designing communication waveforms, the ability of an eavesdropper to correctly demodulate the intended secure signal can be hindered while maintaining successful communications with the desired receiver. This process increases the eavesdropper's bit error rate (BER) and inhibits successful decoding of the secure signal. This method has only been theoretically verified for simple point-to-point channels.

This research will target the design of secure communication waveforms in more complicated and realistic channels such as multipath (fading) channels and multiple antenna environments with multiple possible eavesdroppers. The effects of system constraints such as peak power consumption on the code design must also be researched.

The design of secure wireless channels has primarily focused on encryption, spread-spectrum, and/or beamforming techniques. Achieving enhanced secrecy at the physical layer through the design of communication signals is orthogonal to these existing methods. It has the following benefits:

- Unlike other secrecy techniques that require changes to existing systems such as additional bandwidth or the need for more antennas, this technique can be implemented with minimal changes.
- This method is broadly applicable in all environments.
- This has the potential to improve secrecy in all military and national security wireless communications, including satellite applications, fleet command and control, and even short range tactical communication.

Impact of Materials Processing on Microstructural Evolution and Hydrogen-Isotope-Storage Properties of Pd-Rh Alloy Powders

162522

Year 1 of 3

Principal Investigator: P. Cappillino

Project Purpose:

Palladium and its alloys are optimal storage media for tritium due to high volumetric capacity at low pressure, rapid kinetics of absorption and desorption, and resistance to poisoning. As such, development of synthetic and materials processing methods that yield reliable, optimized material is critical. Preliminary investigation of atomized Pd-Rh powders has shown that post-processing methods have significant influence on the physical properties and dimensions of Pd-Rh powders, which in turn impacts isothermal pressure-composition-temperature (PCT) curves of Pd-Rh materials. These effects are particularly noticeable in the H-storage capacity, plateau pressure slope and hysteresis loop upon H-cycling. The material synthesis and processing methods that have been investigated include gas atomization, cryomilling of atomized powder and electrochemical precipitation. Further investigation using these techniques will be supplemented by spark plasma sintering (SPS) as well as other processing methods to explore the effects of texture and porosity on hydrogen-isotope-storage kinetics and thermodynamics.

In Pd/Pd alloys, the connection between hydrogen-isotope-storage properties and physical properties such as particle morphology, particle size and micro- and nanostructural aspects such as grain size, defect density, and porosity remains to be fully understood. The combination of state-of-the-art facilities for alloy syntheses, a suite of cutting-edge materials characterization techniques, and the ability to measure hydrogen-isotope-storage behavior provides an opportunity to break new ground in understanding this relationship. Feedback between these aspects should facilitate the tailoring of hydrogen-storage properties to suit a given application. The work is in collaboration with UC-Davis.

Developing Software Systems for High-Assurance Applications 164661

Year 1 of 3

Principal Investigator: G. C. Hulette

Project Purpose:

Ordinary development practices for digital logic and embedded sensing and control programs yield unpredictable and unknowable results. While the positive function (what we intend for the system to do) is often at least partially testable, the negative function (what we don't want it to do) typically is not. We must analyze the digital system itself as a mathematical object in order to understand what it is capable of doing under the broad circumstances that high-assurance systems require. Ascertaining negative function is particularly important in high-consequence applications such as nuclear weapons.

Conventional development practices for digital systems yield programs with large spaces of negative function. If code cannot be analyzed, providing assurances against negative function is typically impossible. The research will develop a language in which digital hardware or software can be created that is specifically designed to be analyzable. Writing code in this language is unlikely to be as easy as in an unconstrained language like C, but the results will provably conform to pre-defined surety constraints. Of course, there can be no guarantee of complete safety or security outside of what the designer has specified. However, an important artifact of the methodology is that, even after the digital system is complete and in use, it will remain analyzable. Therefore, a posteriori, newly discovered constraints can still be checked, and in the case that new faults or vulnerabilities are discovered, mitigations can be proven.

Tools for developing formally verified digital systems have the potential to revolutionize high-assurance applications, enabling engineers to hold digital products to an entirely new sort of confidence — the same confidence we place in verified mathematical proofs.

CYBERSECURITY INVESTMENT AREA

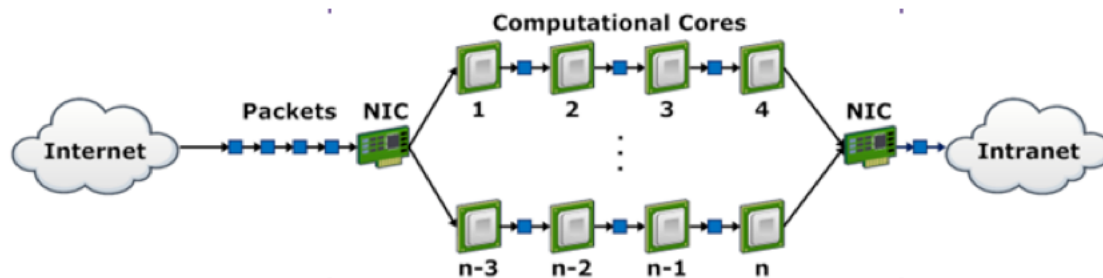
This investment area funds projects designed to improve all aspects of secure computation, including desktop, network, and supercomputing aspects of Sandia and DOE complex operations. This includes both hardware and software projects that hold potential for improving operational capabilities and those designed to detect and thwart malware intrusions into secure and critical cyber systems.

Investigation of the Effectiveness of Many-Core Network Processors for High-Performance Cyber Protection Systems

Project 154198

Network Intrusion Analysis Systems (IAS) and cyber protection devices, such as stateful firewalls, are not keeping up with the explosive growth in network bandwidth. Most of today's systems are barely able to keep pace with network traffic of one Gb/s. Currently, enterprises are moving their networks to 10 Gb/s bandwidths with near-future aspirations of 40 Gb/s. These next-generation networks must be protected with smarter and more efficient cyber solutions to keep pace.

This project turned to many-core processors to solve this growing network bandwidth problem, using a stateful firewall as cyber-protection tool. The project reconceptualized the process of building stateful firewalls in order to demonstrate rapid adaptability and high-performance in the regime of 10 Gbits/s on both 8-core and a 64-core systems. Results included a number of first-time discoveries, including the automation of Juniper rules to Linux IPTables and the demonstration of a pipelined Linux firewall.



Schematic representation of the methodology employed in this project

Cybersecurity Investment Area

Hybrid Methods for Cybersecurity Analysis 154197

Year 2 of 3

Principal Investigator: W. L. Davis, IV

Project Purpose:

The discovery of threats in computer networks is a critical task in cybersecurity. Because of the volume and complexity of the data, most deployed methods rely on signature detection and simple statistics and are guided more by time and hardware constraints than by the needs of the problem. This situation provides an adversary with many degrees of freedom with which to hide.

We propose research that will broaden analysts' views and deepen their capabilities with respect to the always-on torrent of data. We will bridge real-time tools and compute-intensive high-performance computing (HPC) algorithms by allowing the "human in the loop" to transfer insight freely between on- and offline capabilities, thus continually refining their ability to automatically analyze incoming data.

We focus on the following goals:

- Malicious email detection — moving beyond simple signature detection to accurately identify mutations or variations of malicious email attacks
- Malicious behavior detection — aggregating information to detect multistage attacks, analyzing systems for potential vulnerabilities, and detecting rare events.
- Malicious activity attribution — determining the source of malicious code or behavior through analysis of network topology and traffic in the presence of Internet protocol (IP) spoofing, compromised machines and mutating malware.

The challenge of placing the analyst at the center of advanced capability consists in casting each algorithmic component as part of a coherent, accessible whole. Our research will fuse real-time techniques (rule-based intrusion detection and frequent itemset analysis) with large-scale offline methods (graph algorithms, text analysis, and statistical modeling). At a high level, this requires model and data fusion as we enlist diverse algorithms in support of cybersecurity. We find a corresponding engineering challenge as we federate diverse software into a coherent system. Our innovation lies in integrating these parts into a whole that can affect and be quickly affected by expert users and decision makers. Our success will give cyber defenders much of the same agility enjoyed by their adversaries.

Investigate the Effectiveness of Many-Core Network Processors for High-Performance Cyber Protection Systems

154198

Year 2 of 2

Principal Investigator: U. Onunkwo

Project Purpose:

Network Intrusion Analysis Systems (IAS) and cyber protection devices, such as stateful firewalls, are not keeping up with the explosive growth in network bandwidth. Most of today's systems are barely able to keep pace with network traffic of one Gb/s. Currently, enterprises are moving their networks to 10 Gb/s bandwidths with near-future aspirations of 40 Gb/s. These next-generation networks must be protected with smarter and more efficient cyber solutions to keep pace.

New algorithms for smarter cyber protection of high-speed network traffic are being developed that significantly improve the probability of detecting nefarious behavior over the traditional techniques of detecting static signatures or patterns. However, these advanced behavioral analysis techniques require significantly more computational capabilities than static techniques. Moreover, many locations where cyber protections are deployed have limited power, space and cooling resources. This makes the use of traditionally large computing systems impractical for the front-end systems that process large network streams.

In our study, we have pursued application of modern many-core processors to solve this growing network bandwidth problem and have chosen our cyber protection tool as a stateful firewall, a complex streaming network processing tool. We have re-thought the process of building stateful firewalls to demonstrate rapid adaptability and high-performance in the regime of 10 Gbits/s. Our development efforts are being executed on both an Intel 8-core system and a Tiler 64-core system.

Achieving 10 Gbits/s using current many-core systems is ambitious, but demonstrating effective solutions moves us towards a better cyber protection stance. Firewalls are a critical component of Sandia's cyber protection architecture.

Summary of Accomplishments:

1. Demonstrated stateful firewall (IPtables) functionality on single central processing unit (Intel and Tiler processor)
2. Automated translation for converting Juniper Router's rules to IPtables rules
3. Developed fast-processing parallel stateless firewall
4. Demonstrated rates of 10 Gbits/sec on stateless firewall with rigorous testing using Spirent 10G module (www.spirent.com)
5. Developed a fully pipelined stateful firewall (using Linux Netfilter/IPtables); first known existence by team members
6. Automated task balancing in a network processing pipeline

Significance:

Our results demonstrated a number of important developments including some first-time discoveries, namely the automation of Juniper rules to Linux IPTables translation, the demonstration of line rate processing of 10 gigabits/sec network traffic through an extensive list of stateless firewall rules on a many-core Tiler processor, and the demonstration of a pipelined Linux firewall.

This project fits well with the DHS's strategic goal to protect critical infrastructure. It demonstrates a viable way of addressing our cybersecurity needs of reducing vulnerabilities and attacks on our cyber systems that can damage our nation's critical infrastructures. As the nature of adversary cyber tools become more sophisticated and network bandwidth increases to tens of gigabits/sec, it is imperative that cyber protection tools become more flexible, faster, and adaptable to meet the demands of the chaotic world of cyber defense.

Refereed Communications:

R.E. Benner, V.T. Echeverria, U. Onunkwo, J. Patel, and D. Zage, "Harnessing Many-Core Processors for Scalable, Highly Efficient, and Adaptable Firewall Solutions," in *Proceedings of the IEEE International Conference on Computing, Networking and Communications (ICNC)*, 2013.

Leveraging Complexity for Unpredictable yet Robust Cyber Systems

154199

Year 2 of 3

Principal Investigator: J. Mayo

Project Purpose:

Attempts to secure computer systems have consumed decades of effort, resulting in little net progress and a continuing flood of successful attacks. This frustrating outcome strongly suggests that finding a solution requires rethinking the problem and addressing the basic reason that defenders currently cannot ensure security. This reason is the inherent complexity of computer systems, made precise by theorems for which no general algorithms exist for answering questions about the behavior of an arbitrary program. Although engineers try to implement intended behaviors and no others, the theorems imply that unintended behaviors, including vulnerabilities, are generically present and there is no practical procedure for detecting all of them. On the other hand, to compromise a system, attackers need only find a single vulnerability or introduce one—tasks that are quite feasible. Thus, complexity currently gives attackers an asymmetric advantage by affording them a rich environment to exploit vulnerabilities while making protection an effectively unsolvable task.

We are investigating methods for leveraging complexity against attackers so that their task becomes effectively unsolvable, reversing today's asymmetry. We will develop designs, based on diversity and redundancy, for systems that perform their intended function reliably but present a “moving target” to frustrate attackers. Enabling research will focus on automated code transformation, genetic programming, and ways of supporting diversity in compilers, runtime environments, and microelectronics. Our approach aims at generating unpredictability sufficient to thwart entire classes of attacks that rely on implementation incidentals. The strategy applies equally to hardware, software, and the boundaries between them; it will enable fortifying against vulnerabilities heretofore unknown or even introduced subversively. If successful, our work has the potential to alter the balance of power in cybersecurity and restore control to system owners.

Massive-Scale Graph Analysis on Advanced Many-Core Architectures 154200

Year 2 of 2

Principal Investigator: N. L. Slattengren

Project Purpose:

Cybersecurity is a field plagued by “information overload.” Major breakthroughs will require analysts to develop an intuition for massive datasets, empowering them to experiment with unconventional analysis ideas and reduce massive datasets to a set of indicators that a human can absorb and interpret. This will require high-performance analysis tools that can operate at massive data scales. Graph analysis has the potential to be an extremely powerful tool toward this end and has been shown effective in areas such as malware detection and network flow analysis.

Although well suited for massive-scale graph analysis, architectures like the Cray XMT (extreme multithreading) are so expensive that only a handful exist. In contrast, many-core systems are affordable enough to be deployed in the field, enabling in situ data reduction. This could change the face of cybersecurity, particularly in situations when data cannot be securely transported to a central processing location.

This project is geared primarily toward understanding if many-core architectures can be effectively used to tackle the massive-scale cyber data problem. Toward this end, we are identifying the regimes in which a many-core system offers adequate performance and scalability for specific graph analysis tasks and then develop software optimized for these tasks, leveraging Sandia's expertise in graph analysis and multithreaded programming.

The challenge is achieving high performance on a many-core system. Due to the deep memory hierarchy of many-core architectures, the compiler must make reasonable predictions about memory access patterns. Because the memory access patterns of graph algorithms are so difficult to predict, we have crafted our algorithms carefully. Our findings could influence the next generation of many-core designs, improving their viability for this application area in the future.

Secondarily, we propose to identify specific operational cybersecurity concerns that can be addressed using massive-scale graph analysis techniques. Where feasible, we will develop novel analyses and apply them to real cyber data.

Summary of Accomplishments:

Our primary objective was to evaluate the performance of many-core architectures for massive-scale graph analysis. Toward this end, we designed and tested many possible implementations of integer hashing and breadth-first search (BFS) algorithms in order to determine the most scalable solutions for cc-NUMA (nonuniform memory access) architectures. We demonstrated that a 32-core SGI® Altix® UV 10 machine can outperform a 128-processor Cray XMT on hashing at only a fraction of the cost; however, we found the XMT to be the more scalable of the two. Our BFS algorithm scales well on our UV 10 but fails to scale on a much larger UV 1000 due to the deeper memory hierarchy. We also investigated graph compression algorithms that would allow us to process larger graphs and might improve performance on larger-scale systems.

Using what we learned about graph analysis on many-core architectures, we contributed many-core support to two Sandia open-source graph analysis tools, the MultiThreaded Graph Library (MTGL) and MEGRAPHS (Sandia's software package). Because MEGRAPHS allows easy prototyping of parallel

analyses without parallel programming experience, cyber subject-matter experts could use it to experiment with new ideas on full-scale data. This would allow them to more fully understand the characteristics of their data in order to develop a baseline for normal vs. anomalous behavior. We also added many-core support to a tensor decomposition tool.

Toward our secondary objective, we developed an analysis of a distributed data exfiltration attack. The analysis can be used to put an upper bound on how much data could have been exfiltrated in a given period of time by an attacker with limited resources. Additionally, it provides insights into the effectiveness of various mitigation strategies. We also identified several ways that graph analysis has already been applied to the field of cybersecurity, particularly to identifying malware present on a network, and propose follow-on ideas.

Significance:

The size and affordability of many-core systems makes them ideal for performing in situ analysis, allowing cyber data to be processed in situations where the data cannot be transported due to legal, technological, or operational security restrictions. However, many-core systems can also be used at a central location to synthesize data collected from distributed data sources.

Either of these models is potentially of interest for national security missions — that, for example, require analysis of adversarial data, such as in secure operations of DoD or DHS — provided that many-core architectures deliver sufficient computational power. Our results have shown that they do deliver comparable performance to bulkier, more expensive systems like the Cray XMT for properly optimized code.

Proactive Defense for Evolving Cyber Threats 154274

Year 2 of 2

Principal Investigator: R. Colbaugh

Project Purpose:

There is great interest in developing proactive methods of cyber defense, in which future attack strategies are anticipated and these insights are incorporated into defense designs; however, little has been done to place this ambitious objective on a sound scientific foundation. Indeed, even fundamental issues associated with how the “arms race” between attackers and defenders actually lead to predictability in attacker activity, or how to effectively and scalably detect this predictability in the relational/temporal data streams generated by attacker/defender adaptation, have not been resolved. This project is addressing these challenges.

We are characterizing the predictability of attacker/defender coevolution and are leveraging our findings to create a framework for designing proactive defenses for large organizational networks. More specifically, the project is applying rigorous predictability-based analytics to two central and complementary aspects of the network defense problem — attack strategies of the adversaries and vulnerabilities of the defenders’ systems — and using the results to develop a scientifically grounded, practically implementable methodology for designing proactive cyber defense systems. Briefly, predictive analysis of attack strategies will involve first conducting predictability assessments to characterize attacker adaptation patterns in given domains, and then using these patterns to “train” adaptive defense systems that are capable of providing robust performance against both current and (near) future threats.

The problem of identifying and prioritizing defender system vulnerabilities is being addressed using statistical and machine learning to analyze a broad range of data (e.g., cyber, social media) on recently detected system vulnerabilities to “learn” classifiers that predict how likely it is that, and how soon, new vulnerabilities will be exploited. Two cyber threat case studies are being developed and investigated throughout the project, one selected from the cybersecurity research community and one that is more comprehensive and of higher priority to Sandia and to external national security partners.

Summary of Accomplishments:

Our technical approach exploits structure arising from attack-defend coevolution to design predictability-oriented cyber plus social defenses (e.g., predictive, dynamic). Using this approach, we developed: 1) a theoretical framework for designing predictability-oriented cyber plus social defenses and 2) algorithms/case studies for intrusion, spam, phishing, malware, distributed denial of service attacks (DDoS), fraud. We include a few illustrative examples here to highlight sample application areas.

Example One: combine cyber and social models.

Problem: behavior classification, in which innocent and malicious activities are to be distinguished

Approach: predictability-oriented defense

- predictive defense — combine game theory and machine learning (GT + ML) to learn classifiers that predict adversary adaptation in order to counter current and near future attacks
- moving target defense — combine incomplete information game theory and machine learning (HM-HDS + ML) to learn dynamic classifiers that are difficult for adversaries to “reverse engineer”

Example Two: combine cyber and social data.

Problem: timely, reliable early warning for important classes of cyber attacks (e.g., alerting for politically motivated DDoS attacks)

Approach: combine cyber data with social media data.

Additional examples include transfer learning for responsive defense, exploit prediction from vulnerability databases, geographic localization, and dataset curation.

Significance:

We have developed a scientifically grounded framework for understanding/exploiting coevolution of attackers/defenders (predictability-oriented methods, curated datasets) and robust, scalable algorithms for predictive, dynamic, and cyber plus social defenses. This framework and algorithms can directly and significantly benefit DOE, as the security of DOE computer networks is a crucial concern. For example, a methodology for designing proactive GM+ML cyber defenses and algorithms for “standard” threats (e.g., spam, phishing, malware, intrusion) has been demonstrated.

Refereed Communications:

R. Colbaugh and K. Glass, “Proactive Cyber Defense,” Chapter in *Springer Integrated Series on Intelligent Systems*, 2012.

R. Colbaugh and K. Glass, “Early Warning Analysis for Social Diffusion Events,” to be published in *Security Informatics*.

K. Glass and R. Colbaugh, “Web Analytics for Security Informatics,” in *Proceedings of the IEEE Electrical Insulation Conference*, 2011.

R. Colbaugh, K. Glass, and C. Johnson, “Towards Predictive Social Science,” in *Proceedings of the 2012 Winter Simulation Conference*, 2012.

G. Willard and R. Colbaugh, “Understanding Attack-Defend Coevolution for Predictive Analysis and Threat Herding,” in *Proceedings of the 2012 NSA Extreme Cyber Conference*, 2012.

R. Colbaugh and K. Glass, “Predictive Defense against Evolving Adversaries,” in *Proceedings of the IEEE International Conference on Intelligence and Security Informatics*, 2012.

R. Colbaugh and K. Glass, “Leveraging Sociological Models for Prediction I: Inferring Adversarial Relationships, and II: Early Warning for Complex Contagions,” in *Proceedings of the IEEE International Conference on Intelligence and Security Informatics*, 2012.

R. Colbaugh and K. Glass, “Predictability-Oriented Defense against Adaptive Adversaries,” in *Proceedings of the IEEE International Conference on Systems, Man, and Cybernetics*, 2012.

R. Colbaugh and K. Glass, “Predictive Moving Target Defense,” in *Proceedings of the 2012 National Symposium on Moving Target Research*, 2012.

R. Colbaugh and K. Glass, “Anticipating Complex Network Vulnerabilities through Abstraction-Based Analysis,” *Security Informatics*, vol. 1, August 2012.

Detection of Identifiable Data

154532

Year 2 of 2

Principal Investigator: D. Loffredo

Project Purpose:

Loss of data confidentiality is a fundamental risk to any classified program. We do not have adequate tools and techniques to manage this risk. We must investigate new data confidentiality approaches that allow us to detect and attribute data leaks.

Digital content can be copied infinitely and instantaneously. Currently, even when we can detect instances when our electronic information has been compromised, finding the source of the compromise is very difficult. Electronic logs can be easily modified and a skilled attacker may leave no trace.

In previous work, we designed a comprehensive system for detecting and attributing information compromise. This system addresses the complete information life cycle, from creation to destruction. Our system marks data at its inception, which then retains those marks as the data is copied, transmitted, or modified.

The goal of this research is to develop novel, low-overhead methods for detecting previously marked data with little to no impact on system performance. We believe this is important because if system performance is affected by the detector, then users are more likely to attempt to disable it. By limiting our impact on system performance, we hope to improve our detector's availability.

Summary of Accomplishments:

We identified three novel scenarios for preventing and detecting information leaks. The first scenario prevents data leakage between two controlled networks. The second scenario prevents data leakage between a controlled network and a wild network. The third scenario is for detecting leaked data.

Based on these scenarios, we discovered new techniques and developed a suite of tools.

Finally, we demonstrated the viability of our solution by running a live test on live network traffic at Sandia. This proved that our techniques could be deployed at Sandia, at other DOE laboratories, or at other federal agencies.

Significance:

Our major result is a usable product that can be integrated into any organization's network defense, including those of DOE/NNSA and other agencies that require such defenses. This product will improve an organization's ability to ensure data integrity, with little or no impact to end users.

Reliable PUFs for Supply Chain Assurance 154693

Year 2 of 3

Principal Investigator: T. Bauer

Project Purpose:

Supply chain security to prevent, detect, or deter subversion by substitution of networked and stand-alone integrated circuits (ICs) is critical to cybersecurity. Previous Sandia work has leveraged physical unclonable functions (PUFs) as an enabling technology for authentication of ICs throughout the supply chain, which enhances the trust of high-consequence and high-exposure cyber systems by reducing the risk of subversion by substitution. Demonstrating PUF concepts with simple circuits in field programmable gate arrays (FPGAs) or application specific integrated circuits (ASICs) is easy. However, it is difficult to ensure that these circuits exhibit sufficiently high inter-device variation and sufficiently low intra-device variation over a range of environmental conditions. This project is developing methods of consistently achieving PUFs with required variation characteristics in FPGAs and ASICs.

In addition to developing methods for improving variation characteristics, we are investigating antifuses and evolvable circuits to “tweak” PUF output during an “enrollment” operation in the supply chain. Other applications include cryptovvariable generation.

Uncertainty Quantification and Substantiation for Machine Learning in the Context of Cybersecurity

154815

Year 2 of 3

Principal Investigator: M. A. Munson

Project Purpose:

Cybersecurity is critically important in safeguarding the networks that support our national interests. Malware and targeted cyber intrusions constantly threaten to disable major systems, exfiltrate sensitive information, etc. Not only must Sandia protect its own networks, we are playing an increasing role in cybersecurity as it relates to DOE's core nuclear weapons mission and the critical national security missions of other government agencies.

Detecting malware and other cyber threats is difficult due to the massive volume of data. Machine learning has the potential to detect these threats, but it is not widely used because it provides detections without explanations.

The goal of this project is to make machine learning more usable to analysts by quantifying the uncertainty associated with events of interest. Further, this research will add the ability to reach back into the original data to substantiate detected threats with examples of similar past events. This research will lay the groundwork for tools that reduce information overload by allowing analysts to know when they can trust automated analysis tools. This trust comes from providing confidence intervals for individual alarm predictions and from raising warnings when automated analytics are dangerously extrapolating (beyond historical data).

To maintain our strong reputation in cybersecurity, we need to continue to advance the state of the art. Little research has been invested on quantifying the uncertainty in machine learning results and substantiating blackbox outputs because average-case accuracy and reliability is sufficient for most industrial and academic applications. Stronger guarantees are required for cybersecurity and other domains of interest. This project's approach is to develop confidence intervals and extrapolation detection metrics.

Assessing Vulnerabilities of Reconfigurable Logic RF Systems 156250

Year 2 of 2

Principal Investigator: R. A. Bates

Project Purpose:

One of the more common approaches to rapidly identifying vulnerabilities in a system is to use a process called fuzzing. “Fuzz testing or fuzzing is a software testing technique that provides invalid, unexpected, or random data to the inputs of a program. If the program fails (for example, by crashing or failing built-in code assertions), the defects can be noted.” Fuzzing, along with the subsequent debugging and analysis, is commonly used to identify vulnerabilities in computer application programs, device firmware, and device drivers.

Most fuzzing research today is limited to computers, servers, and commercial electronic devices. Many devices are simply never adequately tested for vulnerabilities. This project will instantiate a capability to fuzz some of these less conventional devices, such as radio-frequency (RF) systems utilizing reconfigurable logic field programmable gate array devices.

Summary of Accomplishments:

This project has provided an avenue to understand the fundamental approaches to building fuzzing capabilities through RF channels and has provided steps to develop a more machine-based approach. The goal of the project was to achieve capabilities that could roll into a smarter behavior based system that could more rapidly produce the results necessary to fuzz a system in place.

Significance:

This effort has demonstrated a capability to fuzz digital systems that fall outside traditional cyber systems. This project explored alternative systems that use RF apertures for command and control or other remote sensing systems. The RF aperture of a system allows an alternate entry point and in certain cases an alternate method of vulnerability exposure. This work has provided a capability for the US to analyze (and hopefully patch) critical noncyber RF systems. Its outcomes are of particular interest to agencies such as DoD and NASA whose remote-sensing command-and-control system vulnerabilities must be revealed so that they can be patched or otherwise mitigated.

Peering through the Haze: Privacy and Monitoring in the Cloud Computing Paradigm

156435

Year 2 of 3

Principal Investigator: D. J. Zage

Project Purpose:

Cloud computing is becoming the infrastructure of choice for hosting data and software solutions for many organizations, necessitating the need for research to understand the vulnerabilities of this paradigm. While some security risks, such as the vulnerability of data during transport, are obvious, the infrastructure introduces new non-obvious threats, particularly those due to the lack of control of the physical hardware. These threats pose significant risks to the integrity of data and user privacy during both data storage and data usage. For example, an untrustworthy cloud service provider has access to all of an organization's data stored on the cloud, and it can monitor device usage to further learn about a user. Although some of these risks can be mitigated by leveraging solutions from current research (e.g., cryptographic techniques), creating solutions that maintain the performance and utility of cloud computing while preserving privacy and data integrity remains a challenge. Mitigating these risks is essential for organizations working with sensitive data; failure to do so can result in the compromise of information. This can lead to fiscal loss, embarrassment, and in the case of critical data, even the loss of life.

With the increasing push in governmental sectors towards cloud computing solutions, research is needed in creating solutions that maintain data and user integrity even when considering malicious actors. We are developing a methodology to enable cloud users to store, access, and compute across sensitive data while maintaining security and privacy in terms of the data stored at the provider and in relation to a user's service usage. Our approach will exploit advances in cryptography and communication protocols along with novel uses of the cloud infrastructure to create secure solutions. Additionally, the proposed research will bring us closer to understanding the cloud-computing paradigm in general and further Sandia's leadership in understanding technology critical to the nation.

Secure and Efficient Privacy Preserving Program Obfuscation with Oblivious RAM 156436

Year 2 of 3

Principal Investigator: J. H. Solis

Project Purpose:

Program obfuscation techniques attempt to hide internal instructions or operations from unauthorized observers. However, no existing obfuscator is capable of preventing a dedicated and patient adversary from decompiling and reverse-engineering obfuscated code. All software, from trivial applications to critical infrastructures, is defenseless against a determined adversary.

The ideal obfuscator would transform a program into a virtual black box that, when executed, leaked no information about the underlying program. Unfortunately, early theoretical results have shown that general program obfuscation is impossible. Despite this, alternate obfuscation models have been proposed to investigate scenarios where secure program obfuscation might still be possible. One promising model led to the development of a provably secure code obfuscation technology. However, it is primarily limited to small and trivial programs and extending its capabilities would enable large and complex programs to run securely in untrusted environments while simultaneously protecting against malicious tampering, thereby preserving program integrity.

We propose to investigate new methods that improve overhead and extend general applicability while still preserving cryptographic security and integrity. For example, private information retrieval and oblivious transfer schemes could retrieve program instructions in a secure and private way. Additionally, framing the problem under an oblivious random access machine (RAM) model could securely hide memory access patterns from an adversary. The end result would be a new cryptographically secure, communication-efficient, privacy-preserving program obfuscation scheme. The first phase of this work — incorporating private information retrieval — has already been developed.

Advanced Malware Analytics 157168

Year 2 of 2

Principal Investigator: K. Chiang

Project Purpose:

The malware problem is a difficult problem to solve in today's complex, connected environment where system vulnerabilities are inherent. Malware authors will continue to take advantage of system vulnerabilities as well as human vulnerabilities. Antivirus (AV) and personal security software is abundant (currently 40 companies offer AV solutions) but serve only a best effort at protecting systems and networks. An important strategy to help level the playing field in favor of the defenders is to increase the probability of attribution of bad behavior of an adversary. The Forensic Analysis Repository for Malware (FARM) is a Sandia-developed environment used by network defenders on a daily basis for malware analysis, triage, and threat awareness. FARM automates multiple analysis tools (commercial off-the-shelf [COTS] and government off-the-shelf [GOTS]) to provide incident response analysts with specific details regarding specific malware samples so that they can make more informed decisions about attack software. Though the FARM framework provides a good starting point for defenders to better analyze attack software, more sophisticated adversaries can tailor their malware to thwart analysis techniques making the job of the defender more difficult.

As malware authors develop new tools and techniques for their attack software, the defenders need a way to learn these techniques and ways around them to better analyze the malware. This project continues to advance malware research techniques in three innovative areas that will give the defense new advantage.

Summary of Accomplishments:

We revamped the FARM analysis subcomponents to allow for:

1. fine-grained dynamic analysis
2. scripting capability prior to malware execution for finding trigger conditions of malware
3. better comparison of dynamic analysis modules by removing behavioral noise

We launched a hash sharing service to help tie different federal agencies together to allow for collaboration and sharing, thus decreasing incident response time.

We also implemented a scalable clustering module that can cluster batches of 100 k samples in a day.

Significance:

The work done by this project in advanced malware analytics enables better protection of government systems at Sandia, as well as at DOE and other federal agencies.

Instrumenting Nation-Scale Networks with Hierarchical, Peer-to-Peer Communications

158479

Year 1 of 2

Principal Investigator: T. M. Kroeger

Project Purpose:

From worms like Conficker to network attacks on Estonia and Georgia, the Internet faces large-scale threats that we do not fully understand. Monitoring nation-scale networks requires capabilities beyond that of current systems. At this scale, nodes will randomly come and go and per-node configuration files quickly become intractable. This requires a system that is self-organizing and resilient to failure. Additionally, the volume of events and details can quickly overwhelm any centralized system, necessitating a distributed approach.

The Megatux project has had great success using virtualization to provide a high-fidelity emulation of multi-million-node networks. Yet no existing monitoring system has been able to provide effective instrumentation.

Defending nation-scale networks requires more understanding than we currently have. Understanding these large-scale threats must be preceded by observation of their behavior. This project is extending techniques from distributed system research to create a communications protocol for detailed monitoring within nations-scale networks.

To address the need for a resilient, lightweight, self-organizing network, we will build on existing peer-to-peer communication techniques by adding a network overlay that provides resilient subgroupings and organizes our network. The hierarchy provided by these overlays will enable both data aggregation and regional data evaluation. In this way, we will use the size of the network itself to highlight important information and provide resilience and scale.

We will then deploy large-scale distributed system emulations within Megatux and use our instrumentation to monitor network phenomena at the multi-million-node scale. We will analyze this data for invariants that can be used to identify fundamental behaviors. With information gained from our data analysis we will look to improve our protocol and offer insights for real-time large-scale network forensics.

Memristor Evaluation and Optimization for Cybersecurity

158740

Year 1 of 3

Principal Investigator: M. Marinella

Project Purpose:

Dynamic random access memory (DRAM), static random access memory (SRAM), and Flash memory technologies are nearing physical scaling limits and are beginning to require significant switching energy compared to other components of modern computing systems. Excitement surrounding memristor technology led Sandia to begin investigating possible government applications of this device, which led to the following conclusions: 1) government customers are tremendously interested in using this device for security related applications and 2) we found that these applications require that devices possess several electrical and physical characteristics that are not of interest to companies involved in memristor technology development; thus, they have not been thoroughly studied. In general, these companies consider these requirements to be nuisances — commercial memristor memory is optimized for high density, two-state, uniform operation that is ruined by an irreversible short-circuit state. Sandia has the necessary expertise, infrastructure, and partners to evaluate and optimize this technology and potentially gain significant security-related business.

Sandia is uniquely positioned to carry out this research. We have the necessary facilities and background expertise to fabricate and characterize memristors, a strong partnership and cooperative research and development agreement (CRADA) with leading researchers at Hewlett Packard Labs, and the necessary infrastructure to perform sensitive work related to national security. This work is unlikely to be directly funded by our customers because of its high risk. However, by managing the risk, success in this project would have groundbreaking impact on the design of secure hardware.

A Thin Hypervisor for Dynamic Analysis of ARM^{*} Based Embedded Systems 158742

Year 1 of 3

Principal Investigator: B. K. Eames

Project Purpose:

The center of personal computing is gradually shifting toward commercial mobile devices like smart phones and tablets that act as a window to large scale networked services. Separately, networked embedded control devices are often deployed to sense and manage distributed critical infrastructure. Together, these mobile and embedded devices have tremendous security relevance as they are increasingly used for personal, commercial, and government business. Mobile systems and networked embedded systems have a key similarity. An overwhelming majority of mobile devices and a significant fraction of power-sensitive embedded systems that require high performance are based on the ARM CPU architecture. To understand and counter the threats posed to such devices, one must be able to observe and influence their runtime behavior. The task is not straightforward due to obscurity, limited standards, and intentional removal of debugging and analysis features by manufacturers. This project seeks to build a virtualization-based dynamic analysis platform for ARM-based mobile devices to facilitate security assessment and to serve as the basis for host-based monitoring and intrusion prevention research on mobile and embedded devices. A robust ARM-based dynamic security and analysis platform directly supports Sandia's role in driving innovation in cybersecurity, particularly considering the emerging ubiquity of mobile computing.

^{*} ARM Inc., San Jose, CA

Encryption using Electrochemical Keys (EEK) 158743

Year 1 of 3

Principal Investigator: D. R. Wheeler

Project Purpose:

We are working to develop an alternative method for storing encryption keys on a chip that does not store the information as a bulk charge or a physical deformation, and can therefore, not be interrogated using traditional means. Traditional methods of storing encryption keys rely on techniques that store charge or physically displace an object. Such storage methods are subject to measurement using proper techniques, although these methods usually require invasive processes. The predominant method of storage for keys is electrostatic, where large amounts of charge are needed to create a logical state in memory. This charge is usually written in with milliamps for microseconds, giving rise to nanocoulombs of stored charge. This charge in a square micron gives rise to a significant field, which can be measured in many ways. Alternatively, keys are stored using microelectromechanical systems, but mechanical storage of keys can also be imaged because physical displacements of devices must occur to store key bits.

We are developing an electrochemical set of keys that rely on changes in chemical interaction with surfaces, rather than bulk stored charge. Electrochemical keys will be stored as a liquid phase above a number of differently treated (monolayer) conductors, and the interplay between chemistry and surface will give rise to a chemical potential change. Since this is a surface-only effect, very little charge is stored (femtocoulombs/mm²). Any attempt to read the state of the charge through electrostatic methods will not succeed, as the double layer can be easily disrupted through such methods. Using direct invasive methods to read the charge will result in fracture of the liquid-containing region, and disruption of the key. Under normal conditions, however, the chemical nature of the interface will allow for a very stable voltage to be maintained (such as a battery open circuit voltage, which this structure emulates).

Leveraging Formal Methods and Fuzzing to Verify Security and Reliability Properties of Large-Scale High-Consequence Systems

158744

Year 1 of 1

Principal Investigator: J. Ruthruff

Project Purpose:

The complexity of modern electronics, computer systems, and digital networks has given rise to numerous unintended logic flaws in high-consequence systems, and provided significant space in which adversaries can exploit or hide intentional flaws. Formal methods and fuzzing are widely used to analyze digital designs for flaws that can compromise security or reliability. Formal methods apply advanced logic-based algorithms to rigorously verify the absence of specified flaws in hardware and software systems — offering an improved technical basis for security and reliability assessments. However, the time and space complexity of formal methods scale poorly with increasing problem size, commonly putting realistic high-consequence systems out of reach. For problem sizes too complex for formal methods, the complementary technique of fuzzing (testing with random, but not necessarily unbiased, inputs) is still applicable, but fuzzing cannot guarantee complete coverage of the state space of all but the smallest digital systems.

We are combining both formal methods and fuzzing to analyze large-scale systems by using module-level formal verification to inform system-level fuzzing, thereby increasing the confidence obtainable with fixed computational resources over what could be obtained by either method separately. Another aspect of our research is to combine these two techniques in a parallel setting to further increase the size of the digital systems that can be analyzed. Due in part to noteworthy advances in the underlying research, formal methods have become widespread in recent years and are applied to high-consequence systems ranging from pacemakers to aerospace flight-control systems. Our research will help address the challenges of formally verifying critical security and reliability properties in large-scale cyber systems in Sandia's mission space. In particular, this work will leverage Sandia's high-performance computing (HPC) resources to push the boundary of system complexity that can be analyzed.

Summary of Accomplishments:

Cybersecurity at Sandia has a broad reach across the mission areas of the laboratory. This project team examined two security problems that were designed to provide important insights regarding the applicability of formal verification techniques into these problem spaces. The selected problems were inspired by real problem instances observed by team members in Sandia mission areas. The results provided by these example problems are quantitative, technically sound, and convincing — supporting growing acknowledgment of the applicability of formal methods both internally within Sandia and externally.

This project also explored possible synergy between formal methods and fuzz testing to clarify future research paths in this arena. The results showed that a combination of fuzzing and formal methods can assist a designer's effort to identify the specific flaw responsible for observed erroneous behavior by using formal methods to prune the search space of a fuzzing technique, resulting in a more profitable search space to explore in order to identify the areas of a program responsible for erroneous behavior in terms of flawed design implementation.

Finally, this project identified several opportunities for advancing the scalability of formal verification techniques. Many of these research opportunities are synergistic with Sandia's strengths and targeted to the needs of both the larger research community and the national security interests of the country. One

such approach seeks to address the challenge of composing formal analyses from small portions of a system into a rigorous analysis for the system as a whole. The bottom-up verification methodology would compose the verification of individual components or subsystems into increasingly large assessments until the entire system can be reasoned about in a mathematically sound fashion, given the individual verifications performed at lower levels of the design. This is a research need called out by the White House National Science and Technology Council.

Significance:

This project has positioned Sandia to continue identifying and implementing formal methods for security properties and complex cybersecurity scenarios, given the unique and challenging problem spaces in Sandia's mission areas. There is active interest at present in the ability of formal methods to improve the security and reliability of engineered digital systems — hardware and software — and Sandia is no exception to this trend. Given our areas of expertise, Sandia is well positioned to advance the state of the art in formal methods in the research community in the years to come. Such expertise will be invaluable across DOE and other federal agencies.

Running Malware on Millions of Android Cell Phones

158745

Year 1 of 1

Principal Investigator: J. F. Floren

Project Purpose:

With the rapid growth and availability of smart phones coupled with modern society's dependence on them, it is logical to conclude that cellphones will become a prime target for cyber criminals and nation states. Smartphones are embedded in almost every facet of life, ranging from communication (calls, email, texting, and social networking) to online banking, global positioning system (GPS) navigation, and medical records. Government and industry both heavily rely on smartphones in the workforce, and sensitive information of all kinds resides on and transits them. The number of smart phones sold annually now exceeds the number of desktops and laptops combined.

Security consciousness in the mobile domain lags behind that in the PC world. In a standard computing environment, information can be protected through antivirus software and network monitoring. However, with smartphones the threat model is significantly greater due to the restrictions induced by the platform. Most users have little to no control over the platform and applications. Furthermore, individuals and organizations are severely hindered in their ability to monitor and control the network.

Elcomsoft recently announced that they broke the Blackberry "Secure" backup system and others have reported Android and Apple iOS security exploits. These examples show that the smart phone domain has security vulnerabilities that need to be addressed.

Understanding malware through reverse engineering, sandboxing, and automated analysis, although still not well understood, has become a heavily researched topic in computer security. Cellphone malware, on the other hand, is an area that is virtually untouched. The research that has been done in this area is very minimal and it certainly has not been conducted on a large scale. We will develop tools to boot one million virtual smartphones, mechanisms to introduce and propagate malware, and technologies to monitor cellphone machine state at various entry points. This will create a testbed environment for future research in cellphone security.

Summary of Accomplishments:

We have worked to develop an environment capable of running hundreds of thousands of Android virtual machines in a controlled fashion. This work was initially based on the Megatux emulation platform, which allowed us to boot many virtual machines. Throughout the course of the project, we developed extensions and tools that improved the functionality of the emulation environment, improving the realism and fidelity of the emulation.

One early development was a simulator that would plot the movements of simulated people along the streets of a real city, as obtained from the OpenStreetMaps project. These simulated positions were then provided to a customized GPS driver running in the Android virtual machines. Each phone thus has its own unique and changing position; applications are unaware that the location is artificial. The locations of these devices could be tracked en masse through a Google Maps interface.

Another element was a web interface allowing the user to run the same Android application simultaneously across all virtual machines in the simulation, an important tool for testing.

We created a simulated GSM (global system for mobile communications) modem capable of sending and receiving SMS (short message service) messages by encoding them into a shared database; thus, the simulated phones may send messages to each other.

We also made a demonstration using the Megadroid platform to provide a cloud-like Android service. We wrote software that linked a specific virtual machine to a physical universal serial bus (USB) stick; when the stick was plugged into a computer, a remote session would be opened to that virtual machine automatically, allowing a user to access his resources everywhere. In combination with a password on the virtual machine, this also serves to implement two-factor authentication.

Significance:

Government and industry both heavily rely on smartphones in the workforce, and sensitive information of all kinds resides on and transits them; hence, our work will directly impact improved security within numerous federal agencies. Our work provides a platform to emulate Android cell phones at a large scale, with good fidelity (e.g., location data, SMS capabilities). This enhances the ability of security researchers and applications developers to observe vulnerabilities and test software at scale, without the necessity of maintaining hundreds or thousands of real cell phones as test devices.

Geographically Distributed Graph Algorithms

158746

Year 1 of 1

Principal Investigator: R. D. Smith

Project Purpose:

Graphs are natural models for network and web events in cyberspace. Distributed applications such as online social networks and cloud computing give rise to networks and patterns that are both specific to the communication substrate and geographically disparate. There is interest in modeling and posing queries about behavior in such networks, both individually and as a whole. However, in many cases creating a global model constructed from overlapping subgraphs is not feasible. Graphs may be separated by technical, administrative, trust, or other boundaries, and bandwidth constraints often preclude the data sharing needed to create a global model.

We wish to submit graph queries to these distributed data and to receive answers that would have been obtained using a global model if it were available. Prior work has explored specific graph algorithms over distributed data, but that work does not assume our constraints and employs a different model.

Our project is to develop query and analysis algorithms for distributed subgraphs with overlapping data. We seek to identify the basic primitives necessary to construct and assess algorithms in this environment. Absent a global model, queries may yield a loss of fidelity in the results; an important component is to identify whether this loss can be quantified and to explore whether the extent of the loss can be controlled or predicted. This work is a preliminary exploration of this area, and learning how to formally model and represent the problem is a key component.

Summary of Accomplishments:

This research sought to assess the feasibility of performing cyber-related graph algorithms for an emerging model in which the graph to be analyzed is realized only as a set of independently constructed overlapping subgraphs with limited communication among them. This model is driven by emerging computing trends but has no precedent.

We discovered that graph queries can in fact be posed and algorithms constructed that satisfy the communication constraints of the model. We selected s-t connectivity (given two vertices, find a path between them if one exists) as the motivating algorithm to adapt to the model. We designed an algorithm that finds a path with high probability if one exists across the aggregate of the subgraphs. The algorithm uses only logarithmic communication in a realistic setting. This result updates earlier published results showing that communication across partitioned graphs required log-linear communication for the connectivity algorithm in the worst case. In our algorithm, the communication gains follow directly from leveraging the overlap between the subgraphs.

Our work involved the design and evaluation of multiple computational and communication kernels on top of which the connectivity algorithms were built. These kernels are drawn from algorithmic and statistical concepts including breadth-first search, set intersection, and maximum likelihood estimation. Of the kernels developed, we found that shell expansion (based on breadth-first search) combined with Chernoff-bound arguments provided the best performance, yielding paths with the smallest amount of communication.

This model is novel. Beyond this work, it is the intent and expectation that these kernels, along with others to be developed, will form a core library from which low-communication graph algorithms can be

devised. This work has opened new avenues for research, including understanding and predicting the impact of subgraph overlap, developing and applying new kernels for other graph algorithms, and further enriching the model itself.

Significance:

“Big data” computing and storage trends are driving a model in which data including that for national security is not centrally collocated but is instead distributed across multiple collection facilities. Classic graph algorithms, a mainstay for a variety of cyber-related analyses, are not applicable to this new model.

We have taken the first steps in characterizing this model and understanding its implications. We have developed an initial set of kernels and built from them a first algorithm suitable for analysis. Given the tendency toward increased use of social networking and cloud computing in institutions like Sandia and other federal agencies, this work has direct bearing on national security while simultaneously advancing the state of the art in graph analysis.

Modeling and Development of Nondestructive Forensic Techniques for Manufacturer Attribution 159303

Year 1 of 2

Principal Investigator: R. Helinski

Project Purpose:

The purpose of this project is to develop and demonstrate electronic circuits for counterfeit integrated circuit (IC) detection. Due to the globalization of the IC manufacturing industry, supply chain integrity is a major concern, especially for high-consequence systems. Counterfeit ICs are one of the problems with commercial off-the-shelf (COTS) components. Counterfeit parts have been “knowingly misrepresented”: they have been marked to suit a customer’s order while, in actuality, they are a result of overproduction, recycling or cloning. “Overproduction” describes the situation in which unauthorized copies from the IC fabrication facility enter the market. In “recycling,” ICs are sourced from decommissioned printed circuit boards (PCBs). “Clones” are parts that have been built from the ground up to imitate the genuine product.

Circuits that measure the process variation of an IC could be used as a screening tool that uses electrical characteristics of the IC to indicate that a part may be anomalous. These circuits are well known, however, they have not yet been used in this way. This screen should be able to determine with some level of confidence that a part originated from the expected manufacturer, and perhaps even at the expected time. These tools are suited to serve as a screen because they would be nondestructive, fast, and accurate.

The goal of this research is to identify measurable parameters of manufacturing process conditions and demonstrate the ability to distinguish different component manufacturers. A new IC with embedded circuits for this purpose has been developed and is being fabricated at two distinct facilities. The design of this IC is unique by comparison to other work being done in this area and will have a significant impact because it will add to the comprehensive coverage of the possible solutions to supply chain integrity.

Using Temporal Analysis for Robust Deception Detection 162908

Year 1 of 1

Principal Investigator: R. Colbaugh

Project Purpose:

The primary purpose of this research is to develop a quantitative and systematic approach to detecting and defeating deception. While it may be straightforward for an adversary to distort observables that are directly related to an activity, it is much more difficult to maintain a consistent façade of all indirectly related observables.

Graph analysis, with its emphasis on understanding interdependencies, provides an excellent framework within which to identify and interpret subtle, indirect relationships between entities. While graphs may appear similar in terms of basic graph metrics and topology, for example, having the same number of nodes, similar degree distribution, and similar density, closer inspection may reveal very different connectivity patterns, modularity, and transitivity. These topological differences can be utilized to detect changes related to deception.

Previous research has shown it is difficult to maintain deception over time and we have explored this idea in this research. This temporal-based analysis allows us to track and identify potential reactions to our detection efforts. The ability to identify responses to developed detection mechanisms is critical to the longevity of detection-based security techniques, where entities must not be allowed to subvert or change the detection mechanisms.

Text analytic techniques are exceptionally valuable in the confines of this research and we intend to explore the content collected during the graph generation. We anticipate overlap in content between communities detected in the graph-based techniques and between similar groups. When overlap is not detected, or when unanticipated entities, grammar usage, duplication, or verbiage is found, we can use this data as seeds for further exploration. We will utilize text analytics techniques for establishing implicit relationships between entities based on analyses of the textual content they produce. We will evaluate topology, temporal, and text-based measures for detecting and defeating deception via application to supply chains, e-commerce fraud, and peer-to-peer (P2P) systems.

Summary of Accomplishments:

Objective: develop systematic, scientifically grounded approach to defeating deception.

Approach: dynamic network analysis to exploit deceiver constraints (e.g., strategic/tactical, cognitive/computational).

Accomplishments:

1. Scalable graph-analytic approach to detecting e-commerce fraud.
2. Game-theoretic approach to defeating deception in P2P networks.
3. Social media analytics approach for cyber crime detection and early warning.

Illustrative example: detecting e-commerce fraud

Problem: detect fraudster activity in large-scale e-commerce transaction data.

Approach: network analysis to detect signatures associated with fraudsters attempting to overcome reputation-based security systems.

Sample results:

- Fraudsters form “bipartite cores” with accomplices to establish stable infrastructure with which to artificially boost reputation and defraud users
- We developed and validated scalable algorithms to detect these bipartite cores and associated fraud activity (modularity minimization, transitive clustering analysis).

Illustrative example: characterizing cyber crime via social media analytics

Problem: characterize social media presence of cyber crime activity and evaluate extent to which monitoring online underground markets can help with cyber crime detection/alerting/investigation.

Approach: discovery-oriented content analysis of Web forums employed by cyber criminals for advertising and communication associated with online underground economy.

Sample results:

- Discovered dozens of posts dedicated to underground markets; collected and analyzed ~750 K posts
- Demonstrated predictive power of posts in four high-profiles cases

Illustrative example: defeating deception in P2P networks

Problem: mitigate the effects of deception-based attacks on unstructured multicast networks.

Approach: combine game-theoretic and network dynamics modeling to counter impact of attackers on performance.

Sample results:

- Developed PlanetLab emulation environment within which to conduct experiments with operational multicast systems
- Investigated feasibility of game-based defense against strategic attackers

Significance:

We have developed a scientifically grounded computational methodology for understanding and defeating deception and scalable algorithms for countering effects of deception in various cyber applications (e.g., fraud, P2P, crime).

Multiple government agencies stand to benefit from this work, for example, NNSA, DOE, and DoD. Currently, this work provides algorithms for characterizing deception signatures in transaction/interaction data and deception detection algorithms for large-scale, cyber-related problems. On a one-to-two year horizon, this work enables development of robust systems for detecting/countering deception in high-priority cyber applications.

An Empirical Assessment of the Factors Underlying Phishing 164764

Year 1 of 3

Principal Investigator: M. C. Kimura

Project Purpose:

Traditional approaches to phishing mitigation have largely been unsuccessful. The vast majority of published work has focused either on developing technical solutions that mitigate technical vulnerabilities but still leaves the human aspect vulnerable or on user education. The latter, while appropriate for improving security in the human dimension, assumes that the course material is correct, that users are motivated enough to seek, absorb, and retain the course material, and that the users are engaging in controlled (memory) processing when they encounter phishing attacks. Further research has shown that there is not good consensus on what constitutes correct course material, that user motivation to absorb and retain such material is a poor assumption that some recent work is beginning to address, and that the issue of user controlled processing upon encountering an attack has not been considered at all. Since very different kinds of training exercises may be effective for addressing errors due to controlled processing than for errors due to automatic processing, the last assumption needs to be explored further.

The purpose of the project is to understand the underlying factors that enable compliance with phishing attacks in order to aid in the development of effective anti-phishing training programs. We will begin by addressing the last assumption: whether phishing compliance is linked more strongly to controlled or automatic memory processes. Additional considerations from the fields of prospective memory, retrospective memory, attention, attitude, and motivation will be utilized as appropriate to understand and model the process. Subsequent work will seek to leverage that information to develop effective training.

Machine-Oriented Biometrics and Cocooning for Dynamic Network Defense

164867

Year 1 of 1

Principal Investigator: J. E. Doak

Project Purpose:

Current defenses result in binary access for attackers who have compromised a host on our networks: either the attacker has access equivalent to the most privileged user on that machine, or the intrusion is detected and the machine is removed from the network. This duality is the result of a binary decision as to whether or not the machine is compromised. However, analysts usually make decisions based upon many pieces of data (e.g., artifacts in the web proxy logs) and their experience. We propose to determine if and how this data can be used to progressively and automatically remove a machine from the network without prematurely affecting user experience or allowing an attacker to distinguish between normal network resources and emulated ones.

Previous work on network deception has focused on perimeter detection and low-grade host emulation via honeypots. While this approach may be effective against unsophisticated adversaries, as a national laboratory, we must defend against sophisticated adversaries, usually referred to as advanced persistent threats (APTs). Furthermore, attacks often occur in stages, each of which produces indicators that may be subtle or uncertain but may also be acted upon. Due to this subtlety and the sheer volume of data, human defenders may not always notice these indicators, which motivate using automated tools. Due to this uncertainty, a progressive approach is warranted so as to decisively mitigate risk without interfering with users' work.

Consequently, we propose to build new tools that progressively defend our networks on a machine-by-machine basis using incremental indicators of compromise. We propose using machine uniqueness (machine-oriented behavioral biometrics) for identification and detection and emulating internal services with high fidelity so that attackers are unaware of the deception, are unable to access sensitive information, and waste resources in the attack process. The emulated services will also be instrumented so that defenders can observe attackers and learn about specific APT tools and techniques.

Summary of Accomplishments:

We constructed a prototype system to detect when an attacker is attempting to move laterally on a network from an already compromised host ("pivot machine"). We accomplished this by monitoring a merged representation of both host and network data for an individual host, and then triggering when either a signature-based or machine learning behavior-based event occurs. Triggering sends a message to a cocooning infrastructure identifying a subset of services that are to be switched to their emulated counterparts for the pivot machine. This message may also identify a subset of services to return to normal operation. Emulating services that correspond to the detection event has the effect of denying an attacker access to sensitive information while still allowing later reversion to a completely normal state. Furthermore, we have instrumented the emulated services to monitor attackers more closely than is possible on normal systems. Information obtained from our instrumentation may increase our confidence that an attacker is attempting to move laterally, which may lead us to completely remove the offending host. Conversely, we may determine that the system is behaving normally and restore access to the real services. We believe that machine-oriented biometrics and cocooning present new challenges to APTs by deceiving, delaying, and monitoring their activity.

We created a labeled (i.e., normal or malicious) dataset consisting of host features, generic network features, and protocol-specific network features that are merged by time windows, and generated scripts

to help automate this data collection process. We learned that, with advance warning to operations, future projects can conduct more realistic data generation by using Sandia internal network hosts.

Significance:

We demonstrated proof of concept for machine-oriented biometrics and cocooning, thereby gaining some confidence that these techniques may eventually be operationally viable. This project has helped Sandia establish visibility and a positive reputation in the Dynamic Defense / Moving Target growth area. Its impact will ultimately be felt by DOE and any other federal agency that experiences APTs, which can be assumed to be essentially ubiquitous across federal agencies and laboratories.

Flexible and Scalable Data Fusion using Proactive, Schema-Less Information Services

164869

Year 1 of 3

Principal Investigator: P. Widener

Project Purpose:

Exascale data environments are fast approaching, driven by diverse structured and unstructured data such as system and application telemetry streams, open-source information capture, and on-demand simulation output. Storage costs having plummeted, the question is now one of converting vast stores of data to actionable information. Complicating this problem are the low degrees of awareness across domain boundaries about what potentially useful data may exist, and write-once-read-never issues (data generation/collection rates outpacing data analysis and integration rates). Increasingly, technologists and researchers need to correlate previously unrelated data sources and artifacts to produce fused data views for domain-specific purposes. New tools and approaches for creating such views from vast amounts of data are vitally important to maintaining research and operational momentum.

We propose to research and develop tools and services to assist in the creation, refinement, discovery, and reuse of fused data views over large, diverse collections of heterogeneously structured data. We innovate in the following ways. First, we enable and encourage end-users to introduce customized index methods selected for local benefit rather than for global interaction (flexible multi-indexing). We envision rich combinations of such views on application data: views that span backing stores with different semantics, that introduce analytic methods of indexing, and that define multiple views on individual data items. We specifically decline to “build a big fused database of everything” providing a centralized index over all data, or to export a rigid schema to all comers as in federated query approaches. Second, we proactively advertise these application-specific views so that they may be programmatically reused and extended (data proactivity). Through this mechanism, both changes in state (new data in existing view collected) and changes in structure (new or derived view exists) are made known. Lastly, we embrace “found data heterogeneity” by coupling multi-indexing to backing stores with appropriate semantics (as opposed to a single store or schema).

Training Cyber Situation Awareness in Blue Team Exercises 164894

Year 1 of 1

Principal Investigator: J. C. Forsythe

Project Purpose:

Situation awareness is essential to effective cybersecurity analysis and incident response team performance. However, cyber situation awareness is poorly understood. This project proposes an experiment to help clarify the cyber situation awareness problem, while providing insights that will improve training effectiveness within the context of blue team exercises.

Numerous security technology vendors have offered products to the US Government with the claim they will provide cybersecurity analysts increased situation awareness. However, this cannot be achieved through technical means alone, human analysts must understand the data presented by these new tools, as well as how to effectively apply tools to assess events and develop their response. In the absence of certain fundamental knowledge, there is limited benefit gained from tools intended to improve situation awareness. We hypothesize that analysts need not only an in-depth understanding of the mechanics of the tools, but also a basic understanding of the threat or adversary behavior and tactics.

This project will focus on use of a selected network analysis tool. The tool is being developed at Sandia to aid analysts in identifying and analyzing malicious network traffic. We will train two separate groups in how to use the tool, with one group additionally trained in adversary tactics and techniques. Upon completion of training, participants will be evaluated during a Tracer FIRE (Forensic and Incident Response Exercise) simulated blue team cyber attack scenario. We hypothesize that the group trained in the underlying theory and concepts of the selected tool and adversary attack tactics and techniques will perform better than the groups only receiving training in the mechanics of the tool. Furthermore, the proposed study will provide valuable insights into the optimal depth and duration of training while identifying stumbling blocks in progressing from a novice to an expert user.

Summary of Accomplishments:

Through work on this project, we:

- Developed a methodology and supporting materials for conducting laboratory experiments to measure human performance for cyber operations
- Conducted a laboratory experiment evaluating two alternative modes of training
- Demonstrated that students provided knowledge of adversary tactics and techniques develop a measurably better situation awareness when presented a multi-layered cyber attack
- Found that teams of cyber defenders exhibited asymmetrical patterns of communication
- Found that the personality attributes inquisitiveness and emotional stability and the cognitive aptitude verbal comprehension span predicted individual performance in solving problems in cyber defense

Significance:

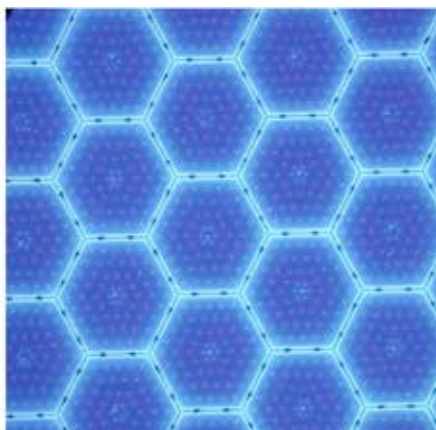
The findings from this study will be applied in structuring future training courses Sandia provides for DOE cyber defenders. Specifically, courses will place an increased emphasis upon knowledge concerning adversary tactics and techniques and developing a narrative to explain the relationships between events. The current study showed that students provided with these skills out-performed students provided equivalent training focused on functional use of software tools.

GRAND CHALLENGES INVESTMENT AREA

Grand Challenge projects are designed to address scientific challenges and urgent national security issues that are broad in scope and potentially game-changing in their impact. As such, these projects require the assembly of often large, always interdisciplinary teams of scientists and engineers, and are commonly funded at an annual level of from \$2M–\$5M. Examples come from areas such as quantum computing, sensor architectures for moment-to-moment surveillance of the environment, nanoscience applications in high-power laser technologies, advanced biological threat detection, and computational approaches to electrical grid reconfiguration to accommodate renewable energy sources.

Science-Enabled Next Generation Photovoltaics for Disruptive Advances in Solar Power and Global Energy Safety and Security Project 159257

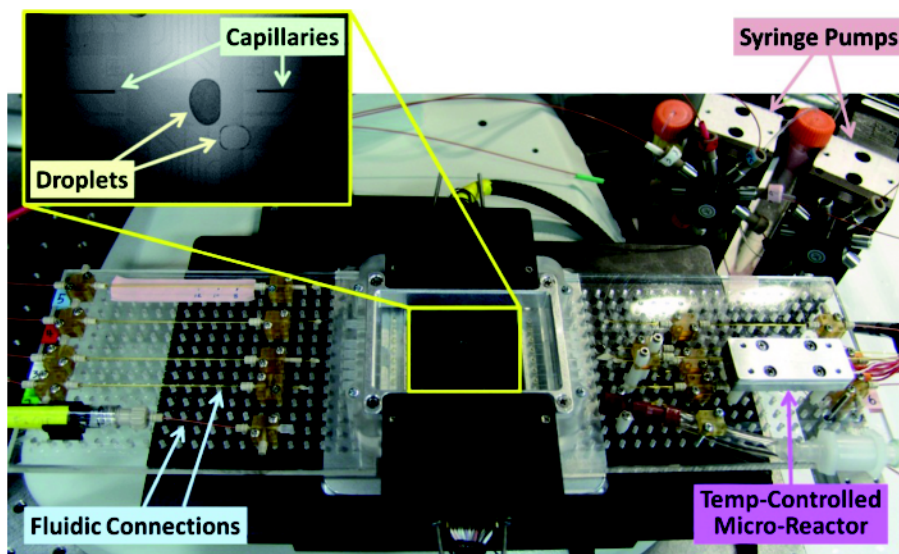
This project is developing solar photovoltaic systems based around the fabrication of microsystem-enabled photovoltaics (MEPVs), >12% efficient solar cells of order 250 μm in diameter and of thicknesses of 15 μm or less. Integrating these unique MEPVs into systems for commercial use will make use of their flexibility; for example, mounted on flexible plastic sheets (such as Mylar), the cells become conformal, able to bend around curved surfaces and to generally conform to irregular surfaces. This gives the MEPV arrays applications that one cannot imagine for other PV cells, for example applied to military clothing to render a soldier energetically independent. And because the many cells can be interconnected in network fashion, rather than via simple serial or parallel connectivity, when placed into more traditional solar-panel arrays (in the tens of thousands of individual cells per square meter), these panels are far more resistant to “opens” or shorts, reducing efficiency by a fraction of a percent rather than potentially inactivating the entire panel. There is also a huge reduction of manufacturing cost because the quantity of the most expensive material component, the semiconductor material, silicon, is reduced to a bare minimum in these ultrathin cells.



Array of MEPV on a plastic sheet being conformally bent around an object

RapTOR: Rapid Threat Organism Recognition Project 142042

Amid concern about bioterrorism threats to national security, there is, in addition to the need for rapid diagnostics for *known* biothreat agents, another requirement to detect, identify, and characterize *unknown* biological threats—that is, pathogenic microorganisms not previously encountered and possibly genetically engineered to increase threat and avoid detection. The technique of Next Generation Sequencing (NGS) enables analysis of such unknown pathogens at the genetic (DNA or RNA sequence) level, but only if a suitable sample of the pathogen’s nucleic acids (DNA or RNA) is available. This is usually not the case in clinical specimens from infected patients, because the pathogen’s nucleic acids exist against the far more abundant and complex background of host (human) nucleic acids. Further compounding the problem is the fact that most clinical specimens are “contaminated” with nucleic acids derived from nonpathogenic microorganisms that live in symbiotic relationships with humans, the “human microbiome.” Thus, when clinical samples are analyzed using a “brute-force NGS” approach (sequencing the entire collection of nucleic acids recovered from a patient sample, for example), the vast majority of DNA and RNA sequences (genetic information) are uninformative, because most belong to either human cells or to the human microbiome, with vanishingly few deriving from the nucleic acids of either known or genetically altered or unknown pathogens. This “needle in a haystack” problem boils down to wasted time and resources, making it highly unlikely that a pathogen’s nucleic acids will be discovered quickly—in time to characterize the nature and biological activity of the pathogen in causing morbidity and mortality in human populations. The goal of this project is to develop and demonstrate new strategies, methods, and technologies for time- and cost-efficient use of NGS for characterization of known and unknown pathogens in clinical samples. To this end, RapTOR has developed a microfluidics-based automated molecular biology (AMB) platform that enables rapid and selective purification, amplification, and formatting of pathogen-derived nucleic acids for NGS analysis. Based around the R&D100 Award-winning digital microfluidic hub, the overall strategy is to deplete nucleic acids of human origin, and those derived from the human microbiome. Accomplishing this, in effect, magnifies any other nucleic acids in a sample collected from a person — that is, those of any pathogenic microorganism that might be present.



Overview photo of RapTOR automated molecular biology platform.

Grand Challenges Investment Area

RapTOR: Rapid Threat Organism Recognition 142042

Year 3 of 3

Principal Investigator: T. Lane

Project Purpose:

Dramatic advances in biotechnology make technical surprise due to genetically engineered bioweapons a growing threat to national security. Our nation is blind to such “unknown” biological agents: its biodefense and public health infrastructure is designed to counteract previously characterized (“known”) pathogens. Modern approaches to discover and characterize unknown pathogens are slow and labor-intensive, requiring specialized laboratory facilities and expertise. They can also be wholly ineffective in identifying pathogens that are non-culturable or unusual.

The Rapid Threat Organism Recognition (RapTOR) Grand Challenge is developing a novel automated molecular biology approach combined with data analysis tools and an informatics architecture to create a new capability—based on ultra high throughput sequencing (UHTS)—to detect and characterize unknown bioagents rapidly enough for decision-makers to effectively respond to an attack or outbreak. The technical challenges include accelerating complex multistep nucleic acid manipulations and re-engineering these processes in an automated and high throughput architecture; developing the capability to process and understand extremely large datasets associated with UHTS; and answering key questions about human biology, such as the level and diversity of microbial loads and host response signatures.

Solving the problem of the unknown biological threat requires a paradigm shift in biodetection: we must create the ability to detect unknowns without a priori knowledge of the agent. The key to this shift will be the integration of several technical innovations in molecular biology, microfluidics, and bioinformatics that will enable UHTS to obtain maximal genetic information from an unknown pathogen in an otherwise overwhelming host background. Because of these capabilities, in the event of an attack with an unknown agent, RapTOR has the potential of preventing mass casualties.

Summary of Accomplishments:

We have implemented a high-throughput bioinformatics pipeline demonstrated to be effective for identification and characterization of pathogens in various clinical sample matrices. We have used the pipeline to analyze hundreds of sequence runs from such samples, and demonstrated state-of-the art performance in our sequence quality control, host background removal, and phylogenetic analysis. A manuscript describing the pipeline is currently under preparation and we anticipate concurrent release of the pipeline software for general use by the sequencing community. We have also implemented hardware and database software for optimal storage and processing of our next-generation sequencing data and analyses.

We have developed and demonstrated hydroxyapatite chromatography (HAC) normalization based suppression and Sandia Digital Microfluidic (DMF) Hub for automated library preparation. An eight-plex HAC platform to fully automate suppression methods has been developed and a cooperative research agreement with the company, Eureka Genomics, has been initiated. The Sandia DMF hub with its modular architecture has successfully executed the Nextera sample preparation protocol for benchtop sequencers. The results and performance of this DMF hub are published in three peer-reviewed papers and a patent.

In the area of molecular biology, the team:

1. Developed second-generation sequencing (SGS) library prep trains for nucleic acids (NA; both DNA and RNA) from blood cells, plasma, and serum, as well as from nasopharyngeal swabs
2. Developed methods for normalization- and capture-mediated suppression of host NA in clinical specimen SGS libraries, for concomitant 10- to 100-fold enrichment of pathogen NA
3. Transitioned library preparation and suppression methods to automated microfluidics-based systems for improved performance (particularly reproducibility)
4. Developed and demonstrated a new informatics pipeline for identification and characterization of known and novel pathogens based on SGS information
5. Used library preparation, suppression, and informatics methods to efficiently identify and characterize pathogens in clinical specimens from subjects infected with unknown pathogens

Significance:

RapTOR will provide Sandia and the nation with a new way to address the serious threat of natural, accidental, or intentional release of unknown biological agents. This is a significant public health and national security problem of interest to a broad array of sponsors and stakeholders, including the Department of Homeland Security, the Department of Defense's Transformational Medical Technologies Initiative, and the National Institutes of Health National Institute of Allergy and Infectious Disease. Strategic plans for these organizations call for new or expanded efforts to address emerging and engineered biological agents within the next five years.

Refereed Communications:

H. Kim, M.S. Bartsch, R.F. Renzi, J. He, J.L. Van de Vreugde, M.R. Claudnic, and K.D. Patel, "Automated Digital Microfluidic Sample Preparation for Next-Generation DNA Sequencing," *Journal of Laboratory Automation*, vol.16, pp. 405-414, December 2011.

N. Thaitrong, et al., "Quality Control of Next Generation Sequencing Library through an Integrative Digital Microfluidic Platform," to be published in *Electrophoresis*.

M.J. Jebrail, M.S. Bartsch, and K.D. Patel, "Digital Microfluidics: A Versatile Tool for Chemistry, Biology, and Medicine," *Lab on a Chip*, vol. 12, pp. 2452-2463, May 2012.

AQUARIUS: Adiabatic Quantum Architectures in Ultracold Systems 152501

Year 2 of 3

Principal Investigator: A. J. Landahl

Project Purpose:

AQUARIUS' vision is to develop a quantum computing architecture whose resource requirements are more achievable than conventional approaches because of the intrinsic noise immunity offered by adiabaticity. A quantum computer is capable of speeding up the solution to numerous problems in our national interest, including those in simulation, energy, and cyber security.

To achieve this vision, AQUARIUS' goals are to experimentally demonstrate an adiabatic quantum optimization (AQO) algorithm in two technologies: 1) neutral atoms trapped in an optical-trap array, and 2) electron spins in semiconductor nanostructures; and for these technologies to 3) evaluate the potential for fault-tolerant universal adiabatic quantum computation (AQC) architectures.

The key experimental challenges are characterizing and adiabatically controlling “always-on” qubit interactions and integrating high-fidelity qubit readout. The key theoretical challenges are developing realistic noise models and adapting fault-tolerance concepts from quantum circuit architectures to AQC architectures.

Previous experimental research has predominantly focused on superconducting-qubit technology, which may not be best suited to AQC architectures. Previous theoretical research has predominantly focused on bringing error correction to AQC instead of AQC to error correction. AQUARIUS will diversify the AQC technology base and explore new ways of making AQC architectures fault-tolerant. This project leverages several unique Sandia capabilities, including the Microsystems and Engineering Sciences and Applications (MESA) fabrications capability (fab), the Center for Integrated Nanotechnology (CINT) fab and High-Performance Computing (HPC) facilities.

Most existing quantum computing efforts are pursuing the quantum circuit architecture, in which an algorithm is expressed as a sequence of simple operations. The price for this simplicity is high—each operation must be error-free to at least one part in 10,000 to operate fault tolerantly. Unfortunately, most groups are so heavily invested in this approach that it requires an LDRD effort to explore alternatives. An experimentally proven resource reduction and a design path forward for scalable universal fault-tolerant AQC could reshape how quantum computing R&D is approached.

Enabling Secure, Scalable Microgrids with High Penetration Renewables 152503

Year 2 of 3

Principal Investigator: S. F. Glover

Project Purpose:

The electric power grid is evolving to a state that has yet to be defined. Unidirectional power and information flow will be replaced by bidirectional flow as new generation sources distribute throughout the electric grid of the future. Renewable and other distributed energy sources cannot be economically and reliably integrated into the existing grid because it has been optimized over decades to large centralized generation sources. Today's grid model is based on excess generation capacity (largely fossil fuel), static distribution/transmission systems, and essentially open loop control of power flow between sources and loads. This leaves the grid extremely vulnerable to terrorist attacks, natural disasters, and infrastructure failures. While developing cost-effective and reliable energy systems has been a concern of both the DOE and the DoD in the past, energy surety —providing cost-effective supplies of energy that are reliable, safe, secure and sustainable—has become increasingly important to both agencies. This presents an exceptional opportunity to introduce and validate the transformational concepts presented in this proposal to impact existing Sandia customers in the DoD as well as the broader national arena.

We are developing a novel, intelligent grid architecture, Secure Scalable Microgrid (SSM), based on closed loop controls and an agent-based architecture supporting intelligent power flow control. This bold approach will enable self-healing, self-adapting, self-organizing architectures and allow a trade-off between excess generation and storage in the grid versus information flow to control generation, power distribution, and loads. Incorporating agent-based distributed nonlinear control to maintain reliable energy distribution while minimizing the need for excessive storage or backup generation will be a revolutionary step towards extreme penetration of renewable energy sources. The development of dynamic nonlinear source models, scalable agent-based architectures, and multi-time-variant simulations will be key components to this solution.

Activity Based Intelligence, Data to Decisions 159214

Year 1 of 1

Principal Investigator: K. M. Simonson

Project Purpose:

In recent decades, the US has invested massively in ground-based, airborne, and space-based sensors and platforms, designed for a wide range of intelligence, surveillance, and reconnaissance (ISR) missions. Together, the sensors generate far more data than can be viewed and evaluated in near-real time. The urgent need for automated techniques to collect, compress, transmit, process, and exploit large data streams is widely recognized throughout the defense and intelligence communities. With deep expertise in sensor physics and design, statistical signal and image processing, high-performance computing, and visual cognition, Sandia is uniquely qualified to play a leadership role in the emerging field of large data analytics. While the overall breadth of the Data to Decisions (D2D) problem far exceeds the scope of a one-year project, this project outlines a research effort that will demonstrate how the complementary strengths of humans and computers can be utilized to enable near-real time analysis of large data sets.

Combining recent Sandia developments in the statistical characterization of human activity based on patterns observed in synthetic aperture radar (SAR) imagery, with carefully designed studies of the analyst-computer interface, the research will enable semi-automated detection of potentially threatening change patterns. The proposed approach of utilizing the context of static, physical scene features along with historical dynamic change models to identify and enhance critical elements extracted from high-fidelity imagery (in near-real time) is entirely novel within the SAR field. The higher-risk and potentially transformative research described here can significantly extend the overall state of the art in SAR processing and exploitation.

Summary of Accomplishments:

The algorithm team developed a robust and automated algorithm for selecting appropriate training data sets used to build statistical models for observed change as a function of time of day and year. We also identified appropriate mathematical transformations to stabilize the variance of the sample coherence function that is used to measure change. We demonstrated the importance of color scale mappings in highlighting anomalous change patterns to human analysts. The human analytics research began with workflow interviews conducted with several analyst teams. Findings from these interviews informed the design of a more formal cognitive task analysis (CTA), which allowed us to characterize the information foraging strategies employed by imagery analysts. To support the quantitative assessment of CTA results, we developed a fully instrumented version of the software used by operational analysts to detect potential threat patterns in near-real time. The combined research clarified the critical role of analyst training and experience in developing complex data products and workspaces.

Significance:

The research conducted under this project helped us to build an interdisciplinary vision for solving complex, high-consequence, and time-critical data analytic challenges. The SAR algorithm work has the potential to enable improved situational awareness across a range of missions that are critical to current and potential future sponsors. And the human analytics research serves as a pathfinder to enable rigorous qualitative and quantitative assessments of the impact of graphical and data analytic strategies on real-time human performance in high-dimensional data spaces.

Science-Enabled Next Generation Photovoltaics for Disruptive Advances in Solar Power and Global Energy Safety and Security 159257

Year 1 of 3

Principal Investigator: G. N. Nielson

Project Purpose:

With the emergence of electric vehicles plugged into our grid, natural disasters that take centralized power plants off-line, concerns about climate change induced by fossil fuel use, and a growing demand for electricity, there is an insatiable need for distributed, point-of-use technologies that generate electricity in a clean, secure, safe, and robust way. However, there are no suitable energy harvesting technologies that meet this need in a way that works as reliably as present-day grid power, at a lower cost than any other energy source.

While solar energy can meet national and global energy consumption with orders of magnitude to spare, the collection and conversion of sunlight to electricity remains two- to three-times more expensive than fossil fuel electricity generation. Unless and until this solar cost barrier is broken, new energy storage and smart grid technologies will not have an enabling, mainstream role to play.

Our team has conceived a photovoltaic system design that consists of microsystems-enabled photovoltaic cells in an independently wired stacked configuration, a microlens concentrator array, optics that enable coarse sun tracking, and massively parallel assembly to produce low cost, packaged solar energy systems. Together, these design elements decrease the need for high-cost photovoltaic (PV) materials by three orders of magnitude, increase conversion efficiency per gram of utilized PV material by a factor of 30, and reduce overall system cost by a factor of 2-3. These components, combined with our new manufacturing and installation concepts, have never been put together into a complete photovoltaic system, but have a real chance of solving all key elements of the solar problem. It is the high cumulative risk, along with the prospect of achieving the elusive solar cost breakthrough that has brought our team to propose this project to design, prototype, and test a complete microsystems-enabled photovoltaic system with the capability to disrupt current fossil fuel and renewable energy generation paradigms.

Extreme Scale Computing Grand Challenge 159258

Year 1 of 3

Principal Investigator: R. C. Murphy

Project Purpose:

Leadership in computing has been a critical factor in our nation's security for the last seven decades. This is particularly true for intelligence, nuclear weapons stewardship, the design and employment of military systems, and the scientific advances that underpin them. US leadership is now threatened by China, which supplanted us on the Top 500 this year. Consequently, the US government, led by DOE, is making a significant investment in exascale technology to ensure overall superiority. This investment rests on Moore's Law, which continues unabated. Energy consumption now constrains the performance of very large scale integration (VLSI) circuits. Without significant innovation, an exascale computer in the 2018 timeframe will consume hundreds of megawatts (MW) (versus approximately five today). Therefore, we propose to address the problem of data movement at all layers of computing from device technology through applications.

We have two overarching goals: first, leverage Sandia's unique capabilities to establish us as the computer architecture leader for the DOE Exascale Initiative, and second, to facilitate the rethinking of Sandia's unique capabilities in computing across the entire laboratory.

Data transport energy will dwarf computation energy. Fixing this requires a rethink of high performance computing (HPC) including finding the most efficient implementation devices, integrating them in a system, and developing new computational models that allow deep but manageable data movement insights. Computational science must shift from minimizing run time to minimizing the entire energy-delay product of an application.

Sandia is uniquely qualified to examine disruptive approaches to creating an exascale system. It alone has the expertise in microelectronic technologies, computer architecture, systems software, and applications that will allow it to pursue the comprehensive atoms-to-applications research needed to overcome the energy challenge posed by data movement in an exascale system. Market forces are directing major computer companies towards hand-held devices and large-scale "cloud" servers, and away from the large-scale tightly integrated systems required for HPC.

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Unpublished Summaries

For information on the following FY 2012 LDRD Projects, please contact the LDRD Office:

Laboratory Directed Research & Development
Sandia National Laboratories
Albuquerque, NM 87185-0123

Project Number	Title
141596	Investigating Payloads and Missions for CubeSat Systems
141597	Laser Characterization and Prediction for Silicon Sensors
141598	Remote Laser Location and Identification
141605	Packaged Integrated Thin Sensor
141690	Nanoparticle Based Filler for Neutron Generator Epoxies
142540	Surety Portal
151269	Cryogenic FPA Optical Interconnects
151273	Nephelae: Harnessing the Cloud
151279	Localized Die Thinning for F/A of Advanced CMOS Designs
151281	Remote Identification and Characterization of Advanced Materials using
151284	Automated Severity Assignment for Software Vulnerabilities
151323	Advanced High Security Command and Control Interface (AHSC2I)
151360	Multi-Phase Laminates: A Study of Prompt Transformations in Abnormal
154273	Beam-Enhanced Electrical Fingerprinting of Complex Integrated Circuits
154763	Coaxial Microwave Neutron Interrogation Source
154778	Advanced Cryptographic Applications
155554	Hybrid Optics for Broadband Optical Systems
156138	Dynamics of Point Source Signal Detection on Infrared Focal Plane Arrays
157310	Optical Refrigeration in Semiconductors for Next Generation Cryocooling
157910	Authorship Attribution for Natural Language Text and Software
158741	Chip Scale Extremely High Data Rate Encryption Architecture Utilizing Novel
158751	Assessment of Windows Integrity Levels for Sandboxed Systems
158754	2-color nBn FPA
158755	Advanced Imaging Optics Utilizing Wavefront Coding
158756	Nanoantenna Enabled Focal Plane Array
158757	Applying Discrimination Methods to Collected and Synthetically Modeled Explosive
158758	Acoustic Detector for Fission Neutrons
158759	Remote Optical Sensing of Ionizing Radiation
158772	Acoustic Tag for Maritime Location and Tracking Applications
158774	Ablation Chemistry Effects on Boundary-Layer Transition
158777	Borazine-Based Structural Materials
158778	Unique Strategies for Radio Frequency Detection
158779	Novel Memory Analyses
158781	Breaking the Language Barrier
158850	Miniature Tritium Free Neutron Generator
158859	New Radiation-Resistant Materials

Appendix A: FY 2012 Awards and Recognition

Award Description	LDRD Contribution
R&D 100 Award, <i>R&D Magazine</i> – Microsystems Enabled Photovoltaics (MEPV): <i>Vipin Gupta, et al.</i>	Project 159257, “Science-Enabled Next Generation Photovoltaics for Disruptive Advances in Solar Power and Global Energy Safety and Security”
R&D 100 Award, <i>R&D Magazine</i> – <i>Neutristor</i>: <i>Juan M. Elizondo-Decanini</i>	Project 158850, “Miniature Tritium Free Neutron Generator”
R&D 100 Award, <i>R&D Magazine</i> – <i>Sandia Cooler</i>: <i>Jeff Koplow, et al.</i>	Project 151304, “Tier 2 Development of Sandia's Air Bearing Heat Exchanger Technology”
R&D 100 Award, <i>R&D Magazine</i> – <i>Sandia Digital Microfluidic Hub</i>: <i>Ken Patel, et al.</i>	Project 142042, “RapTOR: Rapid Threat Organism Recognition”
Brilliant 10 Award, <i>Popular Science</i>: <i>Gregory Nielson</i>	Project 159257, “Science-Enabled Next Generation Photovoltaics for Disruptive Advances in Solar Power and Global Energy Safety and Security,” and others
Presidential Early Career Award for Scientists and Engineers (PECASE): <i>Dan Sinars</i>	Project 141537, “Stability of Fusion Target Concepts on Z,” and others
George Apostolakis Early Career Fellowship Award — International Association for Probabilistic Safety Assessment and Management: <i>Katrina Groth</i>	Project 156135, “Use of Limited Data to Construct Bayesian Networks for Probabilistic Risk Assessment”
Early Achievement Award — IEEE Nuclear and Plasma Sciences Society: <i>Brent Jones</i>	Project 141533, “Advanced K-Shell X-Ray Sources for Radiation Effects Sciences on Z,” and others
Asian American Engineer of the Year: <i>Hongyou Fan</i>	Project 146152, “Scalable Assembly of Patterned Ordered Functional Micelle Arrays,” and others
Asian American Engineer of the Year: <i>Rekha Rao</i>	Project 141508, “Multiscale Models of Nuclear Waste Reprocessing: From the Mesoscale to the Plant-Scale”
Forty under Forty Award, <i>Hispanic Engineer and Information Technology</i>: <i>Bernadette Hernandez-Sanchez</i>	Project 151341, “Advanced High Z NanoScintillators,” and others
Federal Laboratory Consortium Award for Notable Technology Development: <i>Susan Rempe</i>	Project 162035, “Computational Optimization of Synthetic Water Channels”
Excellence in Fusion Engineering Award, Fusion Power Associates: <i>Mark Herrmann</i>	Project 141533, “Advanced K-Shell X-Ray Sources for Radiation Effects Sciences on Z,” and others
American Physical Society Fellow: <i>Mark Herrmann</i>	Project 141533, “Advanced K-Shell X-Ray Sources for Radiation Effects Sciences on Z,” and others

American Society of Mechanical Engineers Fellow: <i>Roy Hogan</i>	Project 15808, “Advanced Materials for Next-Generation High-Efficiency Thermochemistry”
Wilsmore Fellowship, University of Melbourne: <i>Susan Rempe</i>	Project 162035, “Computational Optimization of Synthetic Water Channels”
Best Poster Award – 2012 MRS Spring Meeting: <i>Bryan Kaehr</i>	Project 164677, “Alloys and Composites for Strong and Tough Freeform Nanomaterials”
Best Poster Award — Denver X-Ray Conference: <i>Mark Rodriguez, et al.</i>	Project 151360, “Multi-Phase Laminates: A Study of Prompt Transformations in Abnormal Environments”
Best Student Poster Award — Rio Grande Symposium on Advanced Materials: <i>Lesly K. Vega</i>	Project 151341, “Advanced High Z NanoScintillators”
Best Paper Award — New Mexico Chapter Meeting of the AVS: <i>Nicolas Argibay, et al.</i>	Project 158856, “Synthesis of Wear-Resistant Electrical Contact Materials by Physical Vapor Deposition”
Best Poster Award — International Metallographic Society: <i>Lisa Diebler and Don Susan</i>	Project 151358, “AF&F Fail Safe Feature for Abnormal Thermal Environments Using Shape Memory Alloys”
Best Paper Award — IEEE International Conference on Intelligence and Security Informatics: <i>Richard Colbaugh and Kristin Glass</i>	Project 154274, “Proactive Defense for Evolving Cyber Threats”
WITec Paper Award: <i>D.A. Schmidt, et al.</i>	Project 158829, “Understanding and Exploiting Bilayer Graphene for Electronics and Optoelectronics”

Appendix B: FY 2012 Project Performance Measures

Measure	Number
Refereed Publications	239*
Invited Presentations	322
Technical Advances	145
Patent Applications	59
Patents Issued	41
Post-Doctoral Researchers	118
New Staff Hired from Post-Doctoral Research	17

*CY2012